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IN-SITU TREATING AGENTS

FOR CHEMICAL SPILLS

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IN-SITU TREATING AGENTS FOR CHEMICAL SPILLS

Prepared By

L.B. Solsberg
Hatfield Consultants Limited
West Vancouver, British Columbia

and

A.W. Maynard
ASL Analytical Service Laboratories Ltd.
Vancouver, British Columbia

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Ottawa, Ontario
K1A 1C8

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ABSTRACT

This report provides information concerning various treating agents that were examined for their potential to provide in-situ control of spills of priority substances. Both a literature review and laboratory evaluations were undertaken in order to assess, on a preliminary basis, the use of chelating agents, oxidizers, reducers, precipitants and unique adsorption agents to ameliorate the effects of a range of toxic chemicals.

RÉSUMÉ

Le présent rapport renferme des renseignements sur divers agents qui offrent des possibilités pour l'intervention sur place contre les déversements de substances d'intérêt prioritaire. Afin d'évaluer de façon préliminaire l'utilisation de chélateurs, d'oxydants, de réducteurs, de précipitants et d'agents d'adsorption uniques, capables d'atténuer les effets d'une gamme de substances chimiques toxiques, on a réalisé une étude bibliographique et des évaluations en laboratoires.

FOREWORD

The information contained in this report was prepared by Mr. L.B. Solsberg of Hatfield Consultants Limited, prime contractor for this work, and Mr. A.W. Maynard of ASL Analytical Service Laboratories Ltd. The latter firm acted as subcontractor and conducted all laboratory evaluations. Dr. C. Van Netten of the University of British Columbia assisted in the compilation of toxicological data and chemical reaction theory, and prepared an overview on smectite clays.

The results of this study are preliminary in nature and should serve to provide direction on the future research of in-situ treating agents.

ACKNOWLEDGEMENTS

This project was conducted under the direction of Mr. M.F. Fingas of the Environmental Emergencies Technology Division of the Environmental Protection Service who provided valuable insight into current methodologies for chemical spill control. The suppliers of chemical agents are acknowledged for their provision of technical data included in this report.

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1.0 INTRODUCTION

1.1 Background

Treating agents have been widely proposed in the literature for the in-situ control of spills of hazardous materials. While several reagents have undergone limited laboratory testing specific for toxicity or chemical reactivity, a comprehensive assessment has not been undertaken for many candidate agents which considers a range of practical response concerns. The purpose of this study was to evaluate, on a preliminary basis, treatment techniques commonly referred to in handbooks and other reference documents and potentially applicable to priority substances specified by the Environmental Protection Service (EPS). This should make it possible to discard impractical approaches limited by ambient conditions or other restrictions and concentrate on the further research and development of the most promising agents.

1.2 Approach

Four tasks were planned in order to achieve the objectives of this project:

Task 1 Identification of Candidate Treating Agents
Task 2 Preliminary Assessment of Treating Agents
Task 3 Laboratory Evaluations
Task 4 Analysis of Data, Reporting

Task 1 Identification of Candidate Agents

An initial review was conducted of the literature to determine standard classifications of treatment methods, possible criteria for either rejecting or selecting chemicals for in-situ use, and the specific chemicals which should be examined as initial candidate agents. As outlined in the terms of reference for this work, the following approaches were to be excluded from consideration:

- acid/base neutralizing agents;
- physical agents such as sorbents;
- activitated carbon and charcoal;
- biological agents;
- agents which simply alter the location or state such as simple gelling agents or herders;
- solvents or diluters;
- burning agents; and
- commonly used industrial methods or processes, where the in-situ application would not be new.

This phase of the study involved an examination of manuals, handbooks, technical papers, reports and conference proceedings containing information on chemical spill response and treatment methods. The reference section of the Environmental Emergencies Technology Division (EETD) in Ottawa was consulted. It was determined from this literature search that only a limited number of chemical agents are commonly noted that are outside of the list of exclusions specified in the terms of reference for this study. Most of these are discussed in the Noyes Data Corp. spill cleanup text (Robinson 1979). Furthermore, spill response manuals and handbooks usually advocate the flushing, diking, sorption and/or ultimate physical removal of the spilled material and not so much its in-situ treatment. The exceptions are those spill incidents where neutralization of an acid or base can be readily effected. Nonetheless, candidate agents were identified according to the following treatment approaches as warranting further investigation:

(1) Chelating Agents:
   - .. soluble (sequestrants)
   - .. insoluble (precipitants)

(2) Oxidizing Agents

(3) Reducing Agents

(4) Precipitants

(5) Unique Adsorption Agents

Categorizing agents was found to be an arbitrary process which differs amongst various references and does not usually exclude some overlap of groupings. In addition to the problem of choosing and sorting agents according to specific physical and chemical processes, it was also difficult to ignore the expansive knowledge base recently developed for chemical neutralization methods as well as the application of standard wastewater treatment techniques to spills. Both of these latter approaches, however, were largely excluded from this study as per the directives provided by EETD.

One aspect to which some attention was devoted during the selection process was the applicability of candidate agents to specific priority hazardous substances. Even within the EPS priority lists, toxins were more closely considered in this regard such as cyanides, phenols, aldehydes, metals, etc. rather than the relatively more innocuous materials listed such as sodium chloride and carbon dioxide.

Another component of the selection process was the discussion of candidate agents from different perspectives of individual study team members. In several brainstorming sessions, each person drew upon his or her experience in identifying agents that were (a) amenable to laboratory experimentation, (b) applicable to substances known to pose a significant hazard when spilled, or (c) that would not obviously introduce complications if used at an accident site.

It was at once recognized that while some candidate agents might prove to present difficulties of utilization of one sort or another, several such reagents would be initially considered to result in a more comprehensive and encompassing study. Moreover, the subsequent screening process of the next task would eliminate chemical agents that should not be laboratory tested.

Task 2 Preliminary Assessment of Agents

An assessment of the candidate treating agents was then undertaken according to three aspects of their use, namely, chemical reactivity, toxicity, and field application.

Chemical Reactivity

The interaction between the candidate treating agents and selected priority substances was hypothesized for reactions that go to completion, simultaneous side reactions, and competing and/or reverse reactions. By examining the literature during this phase of the study, major complicating factors became apparent for some reagents. These factors included the formation of unstable compounds, the possibility of violent or excessive reactions, pH adjustments to allow the desirable reaction to proceed, and the effect of other parameters such as temperature, alkalinity, the presence of organics, etc.

Toxicity

Two separate components of toxicity were originally foreseen as requiring examination. These were mammalian and aquatic toxicological assessments. However, it became apparent during the course of the work that water-based spills, and therefore aquatic-related impacts, were the main areas of focus so that terrestrial/mammalian responses to the addition of reagents became less of a concern. Unreacted reagent, predicted end-products and possible by-products were all examined for their potential toxicity.

In spite of this review, a choice will ultimately have to be made on a case-by-case basis as to the advisability of possibly reducing the potential impact of a chemical spill by introducing a reagent that is itself somewhat toxic, albeit considerably less than the substance to which it would be applied.

Field Application

One important aspect of utilizing chemical reagents is the feasibility of transporting and applying them at the spill site. In this regard, the following aspects were examined:

- availability, including grade/purity
- format (gas, liquid, solid, etc.)

- required dosage (or volume)
- physical/chemical properties (solubility, reactivity, corrosivity, affinity for moisture, etc.)
- shelf life, other storage requirements
- safety aspects
- response/reaction time
- application hardware and materials
- cost.

It has been assumed, then, that opportunities might arise to consider the application of reagents, much as neutralization operations have been implemented to control releases of acids and bases. It must, however, be noted that complicating circumstances will occur in spite of this pre-spill investigation of practical aspects. Treatment might not be possible, for example, in the event of a very soluble substance being released into a watercourse; in the case where a high stream velocity quickly transports the material downstream; in the event that it sinks; or where limited access exists. The basic cleanup phases of containment, removal, transfer, storage and/or disposal will still have to be considered in many cases. The presence of organics and suspended sediments as well as other factors such as buffering requirements add further complexities to responding to chemical spills with reagents.

It is therefore most likely that in-situ treatment of a spill will be considered in cases where the released substance has not yet entered a flowing waterway so that time is available to adequately prepare for a response. Preparation should, in fact, include futher preliminary laboratory assessment of the agent and spilled chemical to evaluate its potential effectiveness.

Task 3 Laboratory Evaluations

Once candidate agents had been assigned an overall rating, the design of laboratory experiments was initiated. The experiments were primarily conducted in water-filled glass tanks so that a number of factors were considered, including:

- method of use
- type of spill for which use intended
- "normal" field conditions
- duration of treatment
- recovery of contaminants - if practical.

A typical experimental approach was as follows:

Step 1 - Prepare water to simulate a field station.

- Certain cations and anions were added to create a "typical" hardness and alkalinity.
- Temperature control produced a "normal" field situation, where necessary.
- Dimensions of container were dependent upon spill situation and volume requirements for analysis.
- A sample was taken as a control.

Step 2 - Add contaminant and mix in accordance with type of spill under review.

Step 3 - Carry out the treatment reaction.

Step 4 - Carry out initial analysis for contaminant added to assess immediate effectiveness of treatment.

Step 5 - Remove additional samples over time for analysis of:

- possible by-products
- unreacted agent (if necessary)
- original contaminant to assess stability of complex formed.

NOTE: UV light and aeration were applied to enhance possible breakdown.

Most of the analyses were carried out using:

- Atomic Absorption Spectrophotometry for metals

- Gas Chromatography for organics.

Other water analyses were undertaken to characterize the water before and after treatment, i.e. conductivity, pH, total solids, total organic carbon, major anions and cations, etc.

In some cases, the analytical protocol was tailored specifically to the treatment under review. A more comprehensive indication of test and analytical procedures appears in Section 3.0 for agents which required such work.

Task 4 Data Analysis, Reporting

The final step of this project consisted of reducing all data collected both as a result of the literature review and the laboratory assessments. Rather than organize the study findings according to the above-noted three tasks, information was compiled specific to each of the most promising treating agents or — groupings of agents, in the case of those substances with less potential.

1.3 Report Contents

Section 2.0, Principal Findings, summarizes the study results. It reflects the more detailed review of treating agents comprising Section 3.0. This latter section has been divided into subsections consistent with the categorization of agents presented on page 2. Each subsection, in turn, examines the chemistry, toxicity, field use and, where applicable, experimental methodologies and laboratory evaluation results. The reader is also referred to a concluding, summary subsection for each of the most promising agents highlighting the main conclusions and recommendations. References are included as Section 4.0 while the Appendix lists the priority substances specified by Environment Canada as being implicated in spills.

2.0 PRINCIPAL FINDINGS

2.1 General Findings

The in-situ treatment of hazardous material spills using chemical agents will likely be limited to situations where time allows a proper response to be mobilized, i.e. the contamination is localized, the proposed agent of choice has been laboratory tested on the spilled substance, and the toxicity factor can very probably be reduced.

Environmental factors including pH, hardness, temperature and suspended solids may have significant effects on the efficiency with which a treating agent may react with a toxin as well as on the resultant toxicity of the reaction products.

Many spill treating agents proposed in the literature would not likely prove to be viable alternatives for field application.

2.2 Specific Conclusions

1. The literature cites treating agents without generally undertaking a detailed analysis of the chemistry and/or toxicity of the reaction. The use of many of these agents could result in adverse effects on the environment:

   Oxine to treat spills
   Chlorination to oxidize chemicals
   Sulfide to precipitate metals
   Oxalate to precipitate metals
   Chromic acid as an oxidant

Many treating agents mentioned in the literature are used as reagents in the laboratory but are not readily available for use in a possible field capacity:

Soluble chelating agents such as DTPA, HEDTA, NTA, CTA, etc.
Insoluble chelating agents such as dimethyl glyoxime, cupferron, etc.
Oxidizing agents such as persulfate and potassium ferrate.
Reducing agents such as borohydride.

2. The most acceptable way to treat a heavy metal spill appears to be with EDTA. EDTA forms a stable complex with most metals of concern and the reaction takes place independently of pH. The complex is non-toxic and will not readily break down. It is water soluble and will quickly dilute which may be an advantage or a disadvantage depending upon the circumstances. EDTA is readily available and is relatively inexpensive. It would be effective for the following metals:

Cr, Cu, Ni, Pb, Zn, Cd, Co.

Laboratory experiments were conducted with copper but similar results are expected for the other metals.

3. Another effective treatment for heavy metals is by precipitation. Three precipitates were investigated for copper treatment - sodium carbonate, sodium phosphate and alginic acid. Of these, sodium carbonate was found to be the most effective. It was observed, however, that the precipitate thus formed did not readily settle and had a tendency to dissolve with a pH drop from 8.1 to 5.9. This could be a distinct disadvantage in field use.

Similar problems were observed with sodium phosphate. Alginic acid was not effective and formed a gelatinous precipitate which was difficult to handle.

4. Chemical oxidation can be an effective means of treating certain toxic chemicals and could be particularly useful in the case of a cyanide spill or with specific organic compounds. Two oxidizing agents that were extensively studied were ozone and hydrogen per oxide:

a) Hydrogen per oxide is known to be effective in the oxidation of cyanide, phenol, formaldehyde, sulfide and other toxic chemicals. In reactions with organic chemicals, numerous intermediates are formed as the chemical reaction proceeds to completion. Laboratory tests confirmed the effectiveness of hydrogen peroxide to oxidize phenol. Strict control of variables (especially pH) is necessary and buffering may be required for in-situ utilization.

Hydrogen peroxide is readily available and is not extemely difficult to handle in the field although definite safety precautions are necessary in view of the toxicity of concentrated solutions.

b) Ozone is a very effective oxidant but requires a large, expensive ozone generator to inject this chemical on site. It may be better used as a treatment system to which the contaminant is pumped. It is an effective oxidizing agent for numerous inorganics such as metals and cyanides and many organic compounds. Laboratory experiments confirmed the effectiveness of ozone to oxidize phenol and formaldehyde. Ethylene dichloride, on the other hand, was not effectively oxidized by ozone.

5. Chemical reduction would likely be infrequently required in spill treatment. These investigations showed that the use of a reducing agent would be appropriate for a spill of hypochloride (sodium or calcium). The best reducing agent in such a case would be a sulfite salt (sodium - sulfate, bisulfite or metabisulfite).

6. Smectite clays show distinct promise for use at spill sites. They are inexpensive and not toxic. Due to their high surface area and their chemical reactivity, they readily adsorb metals and certain organic substances. Much more research, however, is required before they can be recommended as treating agents for spills.

7. Laboratory tests could not be conducted that would document the chemistry of the treating agents in all situations. There are too many variables that could be investigated. The experiments, rather, provided a means of confirming or disputing a significant portion of the information in the literature and should form the basis for future work.

8. It is concluded that prior to the field use of treating agents that pilot experiments should be conducted to:

   - confirm that the treatment will work and the end product is non-toxic;

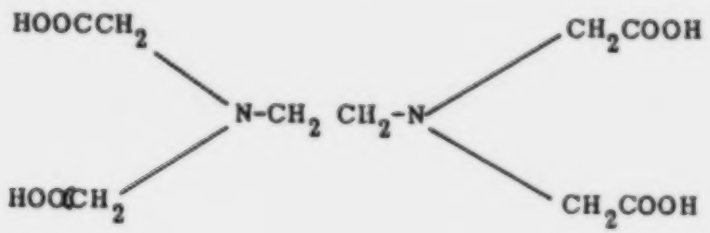
   - demonstrate the need for the control of variables such as pH.

3.0 ASSESSMENT OF TREATING AGENTS

3.1 EDTA

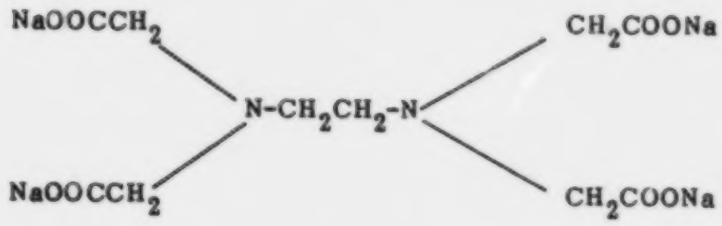
3.1.1 Chemistry

EDTA (or ethylenediaminetetraacetic acid) is an example of a synthetic aminocarboxylic acid with the following chemical structure:



It is usually sold in salt forms, i.e. disodium salt, trisodium salt, tetrasodium salt, and the calcium disodium salt.

The tetrasodium EDTA is most commonly used commercially. The formula is shown below.



The pH and the solubility increase with sodium number. The solubility (20°C) and pH of the free acid are 0.5 g/L and 2.9 respectively. The tetrasodium EDTA, has a solubility (20°C) of 1,100 g/L and the pH of a 1% solution is 11.3.

Reaction with metals is relatively straightforward resulting in a stable complex. The EDTA anion is a hexadentate complexing agent that complexes to a metal by binding its active sites with two N atoms and four oxygen atoms as shown in Figure 3.1-1 below. One EDTA molecule binds with one metal ion.

Figure 3.1-1 Structure of Co-EDTA as determined by X-ray crystallography (Waser 1964).

EDTA reacts with most metals to form stable soluble chelates. The reaction is described as an equilibrium reaction. An equilibrium constant (or stability constant for chelation reactions) is a mathematical expression that relates the concentrations of the reactants and reaction products.

i.e. reaction of Cu and EDTA

$$Cu^{++} + EDTA \longrightarrow CuEDTA$$

$$Ks = \frac{(CuEDTA)}{(Cu^{++})(EDTA^{==})}$$

It is apparent that a higher value for K means a high rate of chelated to unchelated metal in the system. Some K values for metal-chelation reactions (expressed as logarithms) are shown in Table 3.1-1 below.

Table 3.1-1. Log K Values of Metal Chelates of EDTA.

Metal	Log K	Metal	Log K
Fe(111)	25.1	Co(11)	16.3
Cr(111)	23.0	Al(111)	16.1
Cu(11)	18.7	Fe(11)	14.3
Ni(11)	18.6	Cr(11)	13.6
Pb(ii)	18.0	Ca(11)	10.7
Zn(11)	16.5	Mg(11)	8.7
CD(11)	16.4	Na(1)	1.66

From Dean (1985)

If a number of different metal ions are present in a system, the chelating agent will react with the metals in order of decreasing Log K values. If, for example, Fe(111), Cu(11) and Ca(11) are present, any EDTA added will complex the iron first. When the iron is completely tied up, complexing of copper will begin. The calcium will be complexed only if an excess of EDTA over and above that required for both iron and copper is added.

This fact favours the use of EDTA to bind toxic metals in the environment. The most predominant dissolved metals species present in the aquatic ecosystem are calcium, magnesium and sodium. Clearly EDTA will not react with these metals until elements such as copper, nickel, cadmium, lead, etc., are chelated. In fact a pH of 10 or more is required for EDTA to form complexes with calcium and magnesium.

The high log K values demonstrate the stability of the complexes. Aqueous solutions of the acids and the metal salts are stable indefinitely under any temperature attainable at atmospheric pressure. Temperatures of 204 to 232°C (400 to 450°F) may result in decomposition. These solutions are not subject to bacterial or mold breakdown and are unaffected by high acidity and high alkalinity. They are stable to 10% sulfuric acid and to 20% caustic soda, the limiting factor being solubility in these mediums.

Other than complex formation with metals, there are no known "side" reactions.

3.1.2 Toxicity

Toxicity testing of EDTA has usually been conducted in concert with other complexans. Such work has demonstrated the stability of the complexes formed and the environmental protection they afford.

Specifically, experiments clearly show that EDTA and DTPA result in a decrease in the mortality rate in carp (Cyprinus carpio L.) due to the toxicity of 0.5 mg/g Cu in feed No. 4 - Japan Combined Feed Co. (Muramoto 1982). It was found that Cu may increase the amounts of transportation in the viscera by passage through collapsed gill tissue induced by copper sulfate. No deaths were observed in the presence of EDTA or DTPA during the three month (100 day) experimental period of this work.

The inhibition of metal accumulation by the presence of the complexans NTA and EDTA was further determined in carp (Muramoto 1983). There was no significant decrease of mortality of fish due to the toxicity of nickel chloride and sulfate when NTA and EDTA were introduced into the contaminated water.

Other experiments with carp in 5, 10 and 20 ppm chromium chloride and sulfate solutions showed that the addition of complexans (NTA and EDTA) produced decreases in mortality of fish due to the toxicity of Cr(111) in either chromium chloride or sulfate. NTA and EDTA had equivalent positive effects (Muramoto 1981).

Laboratory evaluations of EDTA and NTA have also been conducted to determine the effects of toxicity to carp of aluminum chloride and sulfate at high concentrations (Muramoto 1981a). The EDTA and NTA combined with Al to show a very marked decrease in its content in gills and significant decreases in viscera and other parts. The influence of EDTA and DTPA on the toxicity of cadmium to carp was similarly studied via 100-day experiments which revealed decreases in mortality due to the addition of complexans (Muramoto 1981b). Morphological anomalies (vertical curvature and tail shrinkage of vertabrae) were also reported by the cadmium.

Insofar as the toxicity of EDTA itself is concerned, Clemens and Sneed (McKee and Wolf 1976) found that testing fingerling channel catfish in tap water at 25°C resulted in the following mean threshold limits (TLm):

TLm	24h	167 mg/L
	48h	133 mg/L
	96h	129 mg/L

All fish withstood 100 mg/L; all succumbed at 316 mg/L. These levels represent a significantly lower toxicity factor than the metals to which EDTA would be applied.

3.1.3 Field Use

The use of EDTA to complex metals and thereby inactivate them could be a useful means of spill treatment. Tetrasodium EDTA is the most common form of this material and is sold under a variety of names such as Versene, Trilon B and Questex by manufacturers such as Dow Chemical, BASF, Eastman Kodak and Geigy Chemical. It is available as a liquid concentrate (about 45%) or as a dry powder and costs $1.71/kg in liquid form (Van Waters and Rogers 1986).

The liquid concentrate of tetrasodium EDTA would probably be the most straight-forward to use at a spill site. The liquid could be pumped to the contaminated area or sprayed on the spill at predetermined rates and in measured amounts. This could be done using a tank truck, helicopter-slung bucket, or water-going vessel outfitted with spray gear. Use of aircraft should probably not be considered if precise broadcasting of the concentrate cannot be accomplished, i.e. in areas with dense tree cover or other interferences. Application from fixed facilities such as bridges or other interception points to control spills in rivers is similarly not encouraged since localized fronts of contaminant could quickly bypass such locations.

Utilization of the dry powder format could be considered in the case where mechanical broadcasters or compressed-air powder sprayers are available. This approach could be optimally implemented where a spill has occurred that is localized in a quiescent or slow-moving water body or that is otherwise isolated and distinctly treatable.

After adequate mixing, whatever the application technique finally chosen, complex formation would occur almost immediately. The theoretical amount of liquid EDTA needed to complex various metals is shown in the table below:

Table 3.1-2 Parts of Liquid Tetrasodium EDTA (45% solution) Needed to Complex One Part of Metal

Element		EDTA Requirement
Cadmium	Cd(11)	8.9
Cobalt	Co(11)	17.0
Copper	Cu(11)	15.8
Lead	Pb(11)	4.8
Mercury	Hg(11)	5.0
Nickel	Ni(11)	17.0
Zinc	Zn(11)	15.3

It should be noted that tetrasodium EDTA is alkaline (the pH of a 1% solution is over 11.0). For this reason it was postulated that the misuse of this product could result in an undesirable pH in the receiving environment (Robinson 1979). The disodium salt of EDTA produces less dramatic changes with respect to pH but its low solubility in water may make field use of the product more difficult. Both of these products were investigated further in the laboratory.

Standard safety precautions for chemical use are applicable for application of these products as is discussed in Section 3.1.2.

3.1.4 Laboratory Investigations

A series of experiments was carried out to assess the effectiveness of EDTA to complex copper in solution. Copper was selected because of its acute toxicity to aquatic organisms, in particular fishes. Furthermore, copper sulfate is a commonly transported chemical. The approach and summarized results are discussed below.

Experimental Approach - A series of test jars containing 5 ppm copper (from copper sulfate) solutions were treated with various quantities of disodium and tetrasodium EDTA. The test jars were monitored with respect to pH and aliquots were removed and analysed for complexed copper.

After equivalence point had been established (point at which all the free copper was complexed), a series of experiments was carried out to determine the influence on complex formation of environmental variables such as pH, temperature, water hardness and the presence of suspended sediments.

Results and Discussion - The results of the individual experiments are presented in Tables 3.1-3 and 3.1-4. In the first set of experiments, an equivalence point was established for the complexing of copper with disodium and tetrasodium EDTA. In both cases 10 ml of 0.01 M EDTA solution was found to completely complex all the copper present in the test jar (5 mg Cu^{++} in one litre of water). This quantity compares well with

the theoretical expectation based on a 1:1 ligand-to-metal complex. In the case of the tetrasodium EDTA test, the weight ratio was 8.3 parts ligand to 1 part free copper. If a 45% solution of tetrasodium EDTA had been used, the weight ratio would be 18.8 parts EDTA solution to 1 part copper which is only slightly above the ratios noted in Table 3.1-3.

Table 3.1-3. Addition of EDTA Solutions to Complex Copper.

Amount of EDTA Added to one Litre of Copper Solution	Disodium EDTA		Tetrasodium EDTA	
	pH	Complexed Cu (mg/L)	pH	Complexed Cu (mg/L)
0	4.05	0	4.05	0
2 ml	4.00	1.11	4.72	1.07
4 ml	3.95	2.50	4.38	2.22
6 ml	3.90	3.61	4.20	3.45
8 ml	3.60	4.75	4.11	4.80
10 ml	3.42	4.97	5.68	4.98
15 ml	4.05	5.00	8.46	4.97

Note:

Disodium and tetrasodium EDTA both 0.01 Molar
5 mg/L of Cu^{++} from copper sulfate ($CuSO_4.5H_2O$)
All experiments carried out at room temperature (20°C)

Upon completion of the preliminary experiments, a set of tests was carried out to determine the effects of other variables. These results are presented in Table 3.1-4 and can be summarized as follows:

- A low temperature (4°C) did not affect complex formation.
- pH did not affect complex formation. It was noted that at the higher pH of 7.0 and 8.0, some of the copper precipitated slightly, prior to EDTA addition. This precipitate dissolved, however, after the EDTA was added and all the copper was complexed.

- High hardness did not affect complex formation. Again, some precipitation was evident, probably due to carbonate formation but most of the precipitate dissolved and became complexed after EDTA addition. Calcium and magnesium present in the water did not interfere with the complex formation.
- The addition of river sediment to a test jar removed some of the copper from solution. The free copper remaining was then completely complexed when the EDTA was added. An important observation from all the above experiments was that of pH. Copper sulfate is acidic and the addition of tetrasodium EDTA not only complexed the copper but also neutralized the acidity. Robinson (1979) noted that the disodium salt may be the preferred choice due to pH effects but these experiments along with information noted in Section 3.1.3 concerning solubility and availability indicate that tetrasodium EDTA would be the best choice.

Table 3.1-4. Effects of pH, Hardness, Temperature and Suspended Solids on EDTA - Cu Complex Formation.

TEST CONDITION	pH(*1)	CONCENTRATION OF COMPLEXED COPPER (mg/L)
Basic Experiment (*2)	5.68	5.05
Temperature of 4°C	5.72	4.98
pH Controlled at pH 6.0	6.05	4.95
pH Controlled at pH 7.0	7.11	5.01
pH Controlled at pH 8.0	8.00	5.00
Water Hardness of 100 ppm $CaCO_3$ (*3)	7.71	4.85 (*4)
Addition of River Sediment (4000 ppm)	7.50	3.70 (*5)

(*1) After EDTA Addition

(*2) One litre of Cu^{++} at 5 ppm prepared with $CuSO_4.5H_2O$ and distilled water to which 10 ul of 0.01 m EDTA was added (tetrasodium salt)

(*3) Used well water

(*4) Some copper precipitated due to the hardness of the water and most resolubilized upon EDTA addition.

(*5) Some copper precipitated or bound with the sediment. The dissolved copper before EDTA addition was 3.51 ppm.

3.1.5 Summary

Ethylenediaminetetraacetic acid (EDTA) reacts with metals to form stable complexes in such a way that the more toxic metals form the most stable chelates; this favours the use of EDTA in the natural environment.

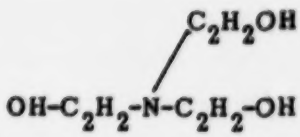
Extensive laboratory testing has also clearly demonstrated that the addition of EDTA to aqueous solutions containing metals significantly reduces the toxic properties of such substances on fish including sublethal effects related to metal accumulations as well as outright mortalities. In field operations, either the liquid concentrate or dry powder format of the tetrasodium salt of EDTA could be applied to mitigate the effects of a spill, subject to circumstances allowing for intimate contact to be made between the treating agent and toxin. Both formats of EDTA are readily available. Disodium EDTA produces less change in pH in the receiving water than its tetrasodium counterpart but its low solubility could limit its effectiveness.

Present laboratory studies have also shown that low temperature (4°C), pH and high hardness do not significantly affect complex formation in the case of either the disodium or tetrasodium salt. This points to the considerable potential of utilizing EDTA compounds for in-situ spill mitigation once quantities have been calculated at which equivalence points will be reached, and knowing that suspended sediments are likely to remove a portion of the metal from solution. This latter phenomenon was also shown to occur under controlled laboratory testing.

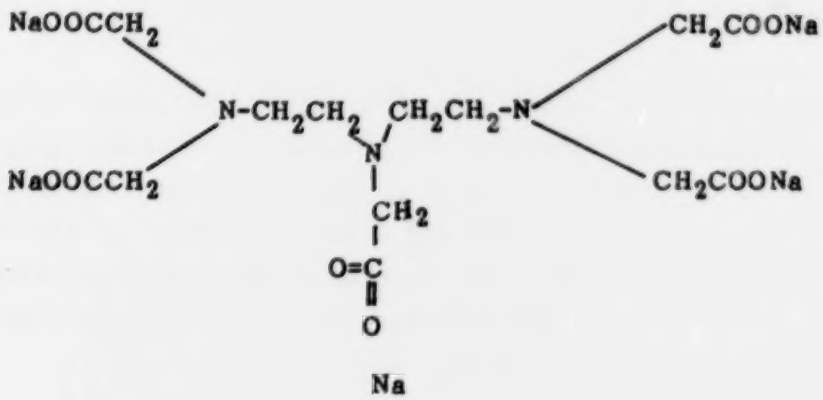
3.2 Other Soluble Chelating Agents

Numerous other chelating agents are available that will form soluble complexes with heavy metals. Some of the more common ones are shown below.

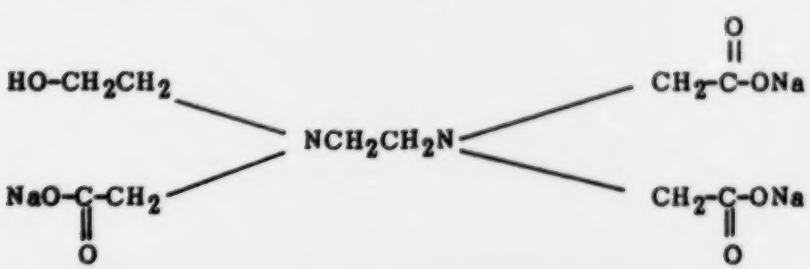
Triethanolamine



DTPA (Diethylenetriamine - pentaacetic acid)



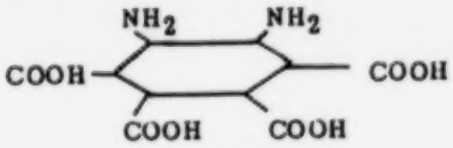
HEDTA (hydroxyethylethylenediaminetriacetic acid)



NTA (Nitrilotriacetic acid)

$$(NH_2CH_2COOH)_3H_2SO_4$$

CTA (diaminocyclohexanetetraacetic acid)



All of these are effective chelating agents and could be considered for spill control. However, there is no discernible advantage that would warrant their use over that of EDTA. In some cases there are even certain disadvantages.

- Triethanolamine is very alkaline and would form complexes that are less stable than EDTA complexes.

- NTA is effective at pH 8.0 or above (Robinson 1979).

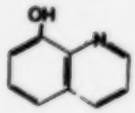
In specific instances, CDTA and DTPA may be slightly more effective complexing agents than EDTA (Dow 1974, Robinson 1979). However, the differences in stability of the complexes are not sufficiently great to be significant. The above chelating agents are not as readily available and are generally more expensive than EDTA. The literature does however, indicate that NTA and DTPA reduce the toxicity of lethal levels of metals to fish (Muramoto 1981, 1981a, 1982, 1983). Water quality criteria (Clark 1980) more specifically ascribe a toxicity factor directly attributable to NTA of 1×10^5 ppb (100 ppm), causing 100% mortality in 7-day tests of American lobsters (homerus Americanus).

Further work on these complexing agents was not undertaken in view of the obvious advantages of EDTA over other chelating agents.

3.3 Oxine

3.3.1 Chemistry

Oxine is an example of an insoluble chelating agent. It is also commonly referred to as 8-hydroxyquinoline or 8-quinolinol. The chemical structure of oxine is:



(C_9H_7NO)

Oxine is essentially insoluble in water or ether but is freely soluble in alcohol, acetone, chloroform, benzene and aqueous mineral acids. It forms chelates with metals forming the complex- $M(C_9H_6NO)n$ where n = valence of the metal ion M. The chelation would occur as a result of activity of the O and N atoms in the molecule as discussed in Section 3.1.1 for EDTA. The resulting complexes are easily formed and stable. Some representative stability constants (see Section 3.1.1 for definition) are shown in the table below.

Table 3.3-1. Equilibrium Constants for Oxine-Metal Complex.

Element	Log K_1	Log K_2
Fe(III)	12.3	23.6
Cu(II)	12.2	23.4
Ni(II)	11.4	21.4
Zn(II)	9.96	18.9
Pb(II)	10.6	18.7
Cd(II)	7.2	13.4

Complex formation with oxine is not particularly sensitive to pH changes, pH 8-9 being the ideal range (Robinson 1979).

3.3.2 Toxicity

The toxicity of oxine by itself is "not great" (Robinson 1979) although water quality criteria refer to a toxicity level of 0.14 ppm for the oxine-Cu complex for salmo gairdnerii (Battelle 1973). Some questions still remain, then, concerning the environmental impact of the required buffer and of the ligand-metal complex. It is known that oxine in the presence of Cu and Fe ions is a powerful bactericide and fungicide which implies high toxicity levels to aquatic microorganisms (Robinson 1979). Additional toxicological data are sparse.

3.3.3 Field Use

Oxine is commercially available and sold under a variety of trade names - 8 Quinolinol, Oxin, Oxychinolin, Quinaphenol, Tumex, 80Q, Bioquin.

While oxine appears to be an effective complexing agent producing an insoluble metal-ligand complex, the product is not practical for use in the field. The main problem is due to its low solubility. The product is usually dissolved in alcohol or acetic acid. It would not be desirable to introduce these carriers to the natural environment as buffering agents.

Oxine has been used to prepare absorbent resins more for use in laboratories to remove metals from reagents or even in the analysis of trace metals in seawater. This approach may be worthy of further examination but at this stage it would appear expensive and would not offer significant advantages over standard ion exchange resins.

3.3.4 Summary

Although oxine is sometimes referred to in the literature as a promising chelating agent for spill treatment, this premise is largely based on its ability to readily form stable complexes with metals. The toxicity of the oxine-metal chelate suggests some limitations for in-situ use. Another main drawback is the alcohol or acetic acid in which it must be dissolved prior to use (due to its low water solubility) and the effect this buffering

component may have on receiving waters. Oxine is therefore not viewed as a practical means of controlling spills in the field as a result of this preliminary examination. The oxine ligand is known for its ability to remove trace metals in seawater on a laboratory scale or in other more controlled situations.

3.4 Other Chelating Precipitants

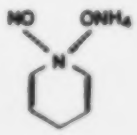
A number of other chelating precipitants are known and discussed in the literature (Robinson 1979; Wheatland et al. 1975; Fletcher 1975) but most have similar limitations as noted for oxine in Section 3.3.

Dimethylglyoxine is widely used in the laboratory to complex metals. The molecule shown here, contains two oxygen and two nitrogen atoms that bind the active sites of the metals.

$$CH_3C{=}NOH$$
$$CH_3C{=}NOH$$

Like oxine, this compound is soluble in organic solvents but is insoluble in water.

Another laboratory agent is cupferron, which is the ammonium salt of N-nitrosophenyl-hydroxylamine.



This compound is water soluble and may be worthy of consideration in precipitating metals by complex formation. It is primarily used as a reagent for copper determinations. Two other laboratory agents used for the complexing of copper are neo-cuproine (2, 9-dimethyl - 1, 10, phenanthroline) and bathocuproine (2, 9, dimethyl - 4, 7 - diphenyl - 1, 10 - phenanthrolinedisulfonic acid, disodium salt).

Numerous other complexes are reported in the literature for use in the laboratory and it was not considered worthwhile to list them all. As a general rule, they are not readily available in quantity, are expensive, and would present critical difficulties in field use at a spill site. Furthermore, little is known about the potential aquatic toxicity of these compounds.

A more promising approach to metal precipitation with chelates was reported by Fletcher (1975) and by Wheatland et al. (1975). These researchers employed the use of four natural polysaccharides - chitin, alginic acid, polygalacturonic acid and starch xanthates, to remove metals from industrial wastewaters.

Comparisons were made between chitin, alginic acid and polygalacturonic acid. All three substances are polyelectrolytes and are similar in structure. They can be described as follows (see also Figure 3.4-1):

- Chitin - flucosamine polysaccharide, similar to celluose. Principal component of mollusc shells.

- Alginic acid - polysaccharide composed of mannuronic acid units linked so that the carboxylic acid group is free. Principal component of kelp (byproduct in the production of iodine from kelp).

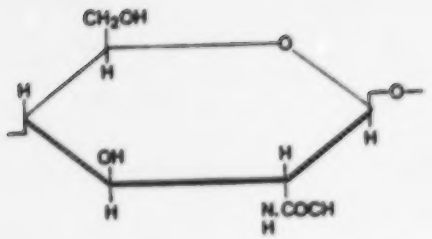
- Polygalacturonic acid - polysaccharide composed of galacturonic acid units. Major component of plant pectins.

The most effective results were obtained with polygalacturonic acid but this product was toexpensive for economic use. Chitin was found to be relatively uneffective.

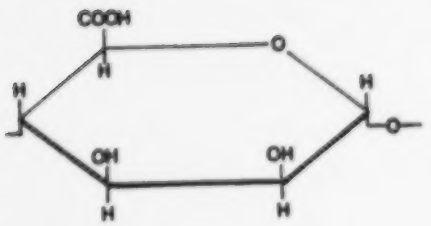
3.4.2 Laboratory Investigation - Alginic Acid

Alginic acid was considered promising enough for further investigation. It reduced concentrations of copper, zinc, nickel and cadmium as follows (from Wheatland et al. 1975).

CHITIN



ALGINIC ACID



POLYGALACTURONIC ACID

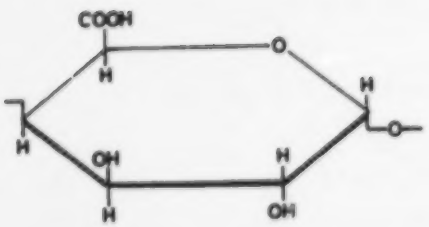


FIGURE 3.4-1 Three natural polysaccharides

Table 3.4-1. Laboratory Investigation - Alginic Acid.

Element	Initial Concentration (mg/L)	Trial Concentration (mg/L)
Copper	55	2.63
Zinc	53	5.89
Nickel	31	4.41
Cadmium	33	1.68

Furthermore, the alginic acid could be regenerated for further use.

The use of alginic acid in spill control does present some difficulties as is noted below.

- The reaction requires a pH of 3.5 to 4.5.
- Calcium and magnesium are also complexed and precipitated.
- The precipitate has a tendency to swell, making final removal difficult.
- The ultimate stability of the complex is unknown. Because it is a natural polysaccharide, microbiological degradation is a distinct possibility.
- The residual levels of metals -noted above - are still sufficiently high to cause toxicity to aquatic organisms.

Alginic acid was evaluated in the ASL laboratory and the concerns noted above were confirmed.

- A 20 ppm Cu^{++} plus 20 ppm Zn^{++} solution was treated with alginic acid producing final concentrations of 2.4 ppm Cu^{++} and 3.6 ppm Zn^{++}. The precipitate formed was gelatinous. The pH before addition of alginic acid was 3.6 and after addition 3.5.

- The above experiment was repeated at pH 5.0 and a viscous solution was formed. Presumably some sodium alginate was formed which is soluble in water and creates an increase in viscosity.

- A 5 ppm Cu^{++} solution was treated with alginic acid producing a final concentration of 1.76 ppm.

3.4.3 Summary

A wide range of chelating precipitants have been investigated by many researchers, primarily for their potential to be incorporated into wastewater treatment processes. Of the substances so examined, alginic acid - a polyelectrolyte - was selected for laboratory assessment in this study. It was determined to present several difficulties as an in-situ spill treating agent, not the least of which would be pH requirements as well as uncomplexed or residual levels of metal that could still have significant toxicological effects on the receiving environment.

3.5 Hydrogen Peroxide

3.5.1 Chemistry

Pure hydrogen peroxide (H_2O_2) is a viscous liquid that boils at 105°C and freezes at 0.89°C. Thus it resembles water in its physical properties and, like water, it is hydrogen bonded. It is relatively unstable with respect to decomposition.

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$

Hydrogen peroxide is soluble in water in all proportions but not in hydrocarbons. Reagent grade, chemically pure H_2O_2 is a solution containing 90% H_2O_2 and 10% water. Commercially it is sold as a 30% solution. To reduce the tendency of H_2O_2 solutions to decompose, storage must be at relatively low temperatures and in light-tight containers. Additives can be used (usually acetaldehyde or sodium stannate) to help counteract catalytic decomposition.

Hydrogen peroxide is a strong oxidizing agent and its major use is in bleaching textiles, synthetic fibres and wood pulp.

In pollution control, the oxidizing capability of hydrogen peroxide is used to eliminate numerous inorganic and organic substances. Cyanide is oxidized to cyanate at a pH of 8.5 to 11.0 (Knorre and Griffiths 1984). Copper is required as a catalyst for this reaction to take place. The cyanate thus formed slowly hydrolyses to form ammonia.

$$CN^- + H_2O_2 \longrightarrow CNO^- + H_2O$$
$$CNO^- + 2\ H_2O \longrightarrow CO_2 + NH_3 + OH^-$$

Metal cyanide complexes can also be oxidized by H_2O_2 and the free metal ions are then precipitated as hydroxides.

$$Me(CN)_4^{=} + 4H_2O_2 + 2OH^- \longrightarrow Me(OH)_2 + 4\ CNO^- + 4H_2O$$

The exception is iron cyanides which are not oxidized by hydrogen peroxides (Knorre and Griffiths 1984).

Sulfide problems (primarily hydrogen sulfide) can be effectively controlled by oxidation with hydrogen peroxide. The reaction takes place at or near neutral pH.

$$H_2O_2 + H_2S \longrightarrow 2H_2O + S$$

Under alkaline pH conditions, sulfate is the end product.

$$4H_2O_2 + Na_2S \longrightarrow Na_2SO_4 + 4H_2O$$

Numerous waste treatment plants employ hydrogen peroxide to reduce sulfide.

Hydrogen peroxide readily oxidizes phenols when the reaction is catalyzed with iron at a pH of 3 - 6. The reaction takes place as progressive oxidation through ring splitting to dibasic acids leading ultimately to carbon dioxide and water (FMC 1983).

$$\text{phenol} + 14H_2O_2 \xrightarrow{Fe^{++}} \text{di basic organic acids} \longrightarrow 6CO_2 + 17H_2O$$

The intermediate compounds are not stable and less toxic than phenol itself.

Aldehydes are oxidized by hydrogen peroxide to produce formic acid and eventually carbon dioxide and water.

$$CH_2O + 2H_2O_2 \longrightarrow [HCOOH + H_2O] \longrightarrow 3H_2O + CO_2$$

formaldehyde — formic acid

Higher aldehydes are similarly oxidized to their corresponding organic acids. In some cases a high or low pH is required.

The use of hydrogen peroxide to treat an actual formaldehyde spill in California was reported by Sikes et al. (1984). Highly contaminated water was collected by a fleet of vacuum trucks and transported to a disposal site where the formaldehyde was oxidized by a caustic hydrogen peroxide process. The remaining contaminated area (wet soil) was treated in-situ by alkaline hydrogen peroxide. First, the ground to be treated was saturated with a buffered (to pH 9.5) solution of sodium hydroxide and soda ash (6,000 gallons). A 5 percent hydrogen peroxide solution (12,000 gallons) was then spread on the same area. After two days the formaldehyde concentration in the soil dropped from 30,000 - 50,000 ppm to about 500 - 1,000 ppm. A biological process was then used to further reduce the concentration to 1 ppm.

Hydrogen peroxide has also been used to enhance bioreclaimation of contaminated sites (Brown et al. 1984). Bioreclaimation takes advantage of the natural ability of common soil bacteria to biodegrade contaminants both in the soil and the groundwater in-situ. Nutrients are required in the form of inorganic salts. Oxygen is also required and has been added by sparging but the solubility of the gas is limited. Hydrogen peroxide provides an ideal supplemental source of dissolved oxygen (one part hydrogen peroxide supplies one-half part oxygen). Laboratory tests have demonstrated that hydrogen peroxide can increase biological activity by several orders of magnitude and its positive effect has been confirmed in field studies.

Hydrogen peroxide is very reactive and will tend to react with any soluble chemical at a lower oxidation state. Therefore, it is often consumed in excess of its theoretical requirement and this must be compensated for by addition to excess. Batch testing to determine demand is recommended.

With complex organic chemicals, there exists the possibility of possible side reactions or the formation of intermediates that may also be of concern environmentally. The reactions are similar to those of ozone discussed in Section 3.6.

3.5.2 Toxicity

Hydrogen peroxide is commonly regarded as a mild disinfectant and is used to counteract various microorganisms (FMC 1983). Dilute solutions are frequently used to cleanse and treat open wounds. While hydrogen peroxide and its primary decomposition products for simple organics (oxygen, carbon dioxide and water) are not systemic poisons, concentrated solutions (H_2O_2 is shipped in aqueuos solutions varying from 27.5% to 98% (Environment Canada 1984)) irritate human skin, particularly sensitive tissues such as mucous membranes and the eyes. Furthermore, direct ingestion can be highly toxic as follows:

Threshhold Limit Value (TLV), inhalation = ppm; 1.5 mg/m^3
Short-term Inhalation Limits = 2 ppm; 3 mg/m^3 (15 min.)
Lethal Concentration 50 (LC_{50}), inhalation, rat = 2,000 mg/m^3/4h (90%)
Lethal Dose 50 (LD50) skin, rat = 4.06 g/kg (90%)

In laboratory studies in which hydrogen peroxide has been introduced at concentrations greater than 40 mg/L, it has been determined to be toxic to fingerling trout (McKee and Wolf 1976). In such bioassays, concentrations less than 40 mg/L were found to produce no harmful effects over a 48-hour test period. In summary, then, hydrogen peroxide itself is highly toxic when consumed internally but tends to be more innocuous in the aqueous environment particularly if it has reacted to completion with simple organic compounds.

3.5.3 Field Use

Hydrogen peroxide is usually sold as a 30% solution or as a 70% solution in drums (200 litre) or tank trucks (15 m^3). The storage vessels are equipped with a venting device. Extreme care is required in transportation (in accordance with the manufacturer's specifications).

Compatability is important in storage, the most practical material being high purity aluminum alloy. Type 316 stainless steel is a satisfactory material for transfer pumps. It is best to store H_2O_2 in containers supplied by the manufacturer.

Decomposition, caused by contamination, liberates oxygen and heat. Therefore, all handling procedures should be directed towards maintaining the purity of the product. H_2O_2 is not considered to be explosive. However, when mixed with organic and metal catalysts explosive conditions can be created.

Rubber gloves, eye protection and suitable protective clothing should be worn when handling hydrogen peroxide. First aid measures should be well known by those handling the product.

Should field treatments of hydrogen peroxide be considered, laboratory pretesting is recommended so that the amount of buffering required is known for the specific toxin spilled. This may not always be possible. Applications, where feasible, should then take place using a metered/controlled pump so that inhalation and/or skin contact is absolutely avoided. Use of hydrogen peroxide should only be planned in cases where the spilled contaminant is localized and intimate contact with it is assured. Its water solubility should, however, enhance its potential to be effectively used.

3.5.4 Laboratory Investigations

Experiments were carried out to investigate the oxidation of phenol with hydrogen peroxide. Phenol was selected for these experiments because of its prevalent use in industry, its solubility in water and its toxicity to fish. Also, information is widely available in the literature on which the experiments could be based.

Experimental Approach - A phenol solution (20 ppm phenol) was prepared using distilled water. The basic experiment was as follows:

- One litre of phenol solution was prepared.
- Ferrous sulfate was added (0.120 g to give a Fe^{++} concentration of 25 mg/L).
- Hydrogen peroxide was added - 0.3 ml of 30% H_2O_2 to give a peroxide/phenol weight ratio of 4.5/1 which is a significant excess.
- This experiment is designated as Test 3 (see Table 3.5-1).

Table 3.5-1. Oxidation of Phenol By Hydrogen Peroxide.

Test Condition	pH (during reaction)	Final Phenol Concentration (mg/L)
Original Phenol Solution	2.80	20.0
Test 1 - Fe^{++}	2.95	20.0
Test 2 - H_2O_2	2.85	18.2
Test 3 - Fe^{++} + H_2O_2	3.11	L0.20
Test 4 - Fe^{++} + H_2O_2 + pH to 6.0	5.91	17.1
Test 5 - Fe^{++} + H_2O_2 + pH to 5.5	5.35	9.2
Test 6 - Fe^{++} + H_2O_2 + pH to 5.0	5.01	2.0
Test 7 - Fe^{++} + H_2O_2 + pH to 4.5	4.51	0.5
Test 8 - Fe^{++} + H_2O_2 + pH to 4.0	4.06	L0.2
Test 9 - Fe^{++} + H_2O_2 + pH to 3.5	3.60	L0.2
Test 10 - Fe^{++} + H_2O_2 + pH to 4.5, 5°C	4.51	0.8
Test 11 - Repeat Test 10 but suspended solids (4,000 ppm added)	4.65	0.9

L = less than (not detected).

Control experiments were carried out, one without the addition of hydrogen peroxide (Test 1) and one without the addition of the iron catalyst (Test 2).

Because of the low pH of the reaction (pH 3.11 during the basic experiment Test 3), the experiment was repeated but with the pH adjusted to 6.0. Oxidation of the phenol did not take place, indicating a dramatic pH dependence. Further tests were carried out to document this pH effect over a wider pH range (Test 9); the results show that the optimum pH is in the 3 to 4.5 range (see Figure 3.5-1).

The effect of temperature and suspended solids (4,000 ppm) was also assessed and found not to interfere significantly with the reaction of hydrogen peroxide oxidation of phenol.

3.5.5 Summary

Hydrogen peroxide is a powerful oxidizing agent that is readily available. It has been used to treat a wide range of chemical compounds including both organics and inorganics in controlled, plant situations and, albeit very infrequently, in spill incidents. Extreme caution must be exercised if hydrogen peroxide is contemplated for in-situ treatment, especially as regards avoidance by personnel of skin contact, inhalation and ingestion of concentrated solutions. Use of hydrogen peroxide is foreseen on localized releases where time permits the predetermination of steps that should be taken to buffer the reaction in view of its critical dependence on pH. Sudden additions of hydrogen peroxide should be avoided in order to avoid excessive, violent reactions.

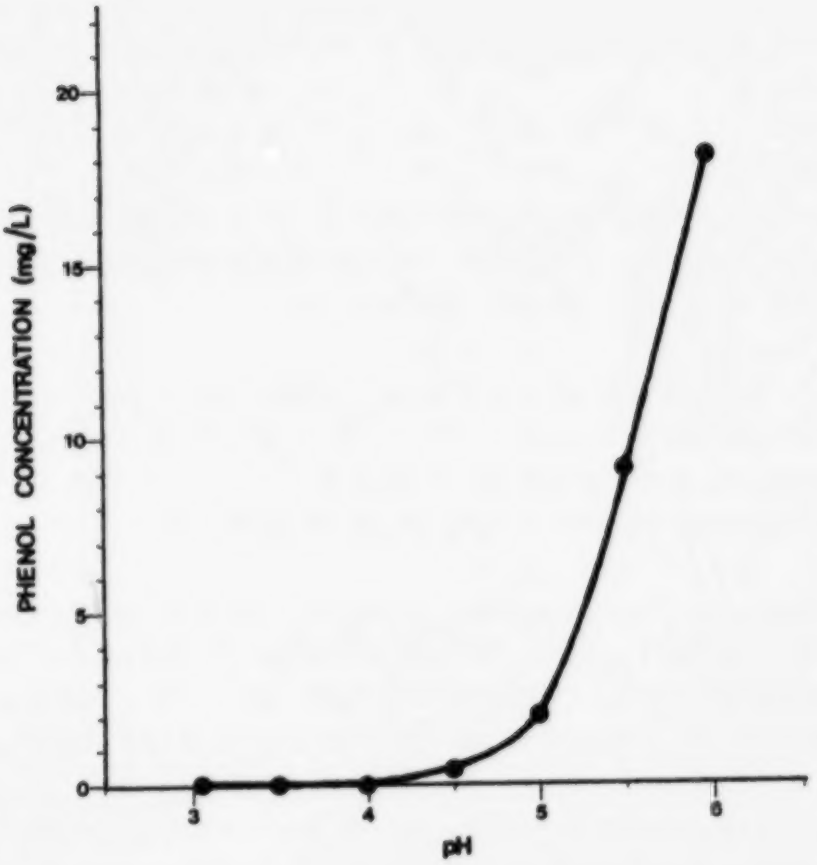
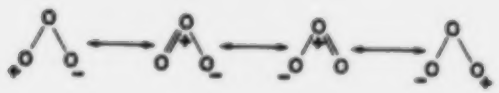


FIGURE 3.5-1 Effect of pH on peroxide oxidation of phenol

3.6 Ozone

3.6.1 Chemistry

Ozone is an allotrope of oxygen and is composed of three oxygen atoms arranged in a chain. The resonance structures of the ozone molecule are:



At atmospheric pressure and temperature, ozone is a colourless gas. The human olfactory organs are extremely sensitive to this gas and concentrations as low as 0.5 ppm can be detected. The odour resembles sulfur dioxide.

Ozone is naturally formed in the upper atmosphere by absorption by oxygen of ultra-violet (UV) radiation (213.7 nm). At 20,000 to 40,000 metres the concentration of ozone can be as high as 5 - 10 ppm. It is this absorption of UV light in the atmosphere that prevents such radiation from harming life on the planet's surface.

The common commercial method of ozone production utilizes an ozonizer or ozonator which produces 0_3 using a silent arc discharge. In general, all ozonizers consist of a pair of electrodes, a layer of insulation, an air space and a source of high-voltage alternating current. Air or oxygen is used to remove the ozone as it is formed.

Ozone is highly destructive to many organisms such as bacteria, fungi and algae and it is finding increasing use in water treatment plants. Concentrations of less than 1 ppm will sterilize water.

Ozone is a powerful oxidizing agent, exceeded only by fluorine in oxidation potential. It oxidizes most inorganic ions to their final oxidative state. In fact, ozone has been used commercially to remove excess iron, manganese, and other metals from water supplies.

$$2\,Fe^{++} + O_3 + H_2O \longrightarrow 2\,Fe^{+++} + O_2 + 2OH^-$$

$$Fe^{+++} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$$

$$Mn^{++} + O_3 + H_2O \longrightarrow Mn^{++++} + O_2 + 2OH^-$$

$$Mn^{++++} + 4OH^- \longrightarrow Mn(OH)_4 \longrightarrow MnO_2 + 2H_2O$$

Many other inorganic ions can be oxidized by ozone such as nitrite to nitrate and sulfite to sulfate.

In aqueous solution, ozone oxidizes cyanides to cyanates by an extremely rapid reaction.

$$CN^- + O_3 \longrightarrow CNO^- + O_2$$

The toxicity of cyanates is only 1/1,000th that of cyanides and they can easily be decomposed biologically to NH_3 and CO_2.

Further oxidation to completion takes place more slowly and requires a higher concentration of ozone:

$$2OCN^- + H_2O + 3O_3 \longrightarrow 2HCO_3^- + 3O_2 + N_2$$

Cyanates also decompose on hydrolysis, for which ozone is not required. The following reactions are possible:

$$OCN^- + 2H^+ + H_2O \longrightarrow CO_2 + NH_4^+$$
$$OCN^- + 2H_2O \longrightarrow HCO_3^- + NH_3$$
$$OCN^- + NH_4^+ \longrightarrow NH_2COHN_2$$

At room temperature the last reaction is shifted strongly towards the formation of urea, which is converted into ammonium carbonate in the presence of urease enzyme (i.e. microbiological degradation).

$$2H_2O + NH_2CONH_2 \longrightarrow (NH)_2CO_3$$

By the action of excess of ozone, the full oxidation of urea also takes place:

$$NH_2CONH_2 + O_3 \longrightarrow N_2 + CO_2 + 2H_2O$$

Oxidation by ozone can be carried out in packed absorption columns of small space requirements and ozone addition can be controlled by measuring the redox potential. The pH must be set by NaOH to a minimum value of 9.

According to the investigation of Kandzas and Molina, the rate of oxidation $CN^- + O_3 \longrightarrow CNO^- + O_2$ is independent of pH in the pH range of 10.5 to 12 and the ozone demand corresponds to stoichiometric. By increasing the pH, the rate of reaction strongly rises along with the rate of ozone decomposition. Thus for further oxidation a substantially higher ozone consumption results than would be required according to the equation:

$$2CNO^- + 3O_3 + 2OH^- = 2CO + N_2 + 3O_3 + H_2O$$

The above reactions demonstrate the need to add an excess of ozone in order to oxidize the intermediate reaction products to their final oxidation states. This is common of most oxidation reactions.

In reactions with inorganic compounds, oxygen is a reaction product. Organic reactions are much more complex in that the ozone molecule becomes coupled to the organic compound to form an ozonide. An ozonide is an intermediate reaction product and is often unstable and is subsequently hydrolized to give degradative products. Because of the complexity of the reactions it is often difficult to predict the various side reactions and all the end products. A good example is the ozonation of phenol which is a commercially used procedure. Eisenhauer (1986, 1971) determined the pathway for phenol ozonation depicted in Figure 3.6-1.

Excess ozone can promote the oxidation of the phenol reaction products to finally form carbon dioxide and water. In practice, however, excess ozone is not applied and complete oxidation does not take place; toxicity is significantly reduced in all uses and the

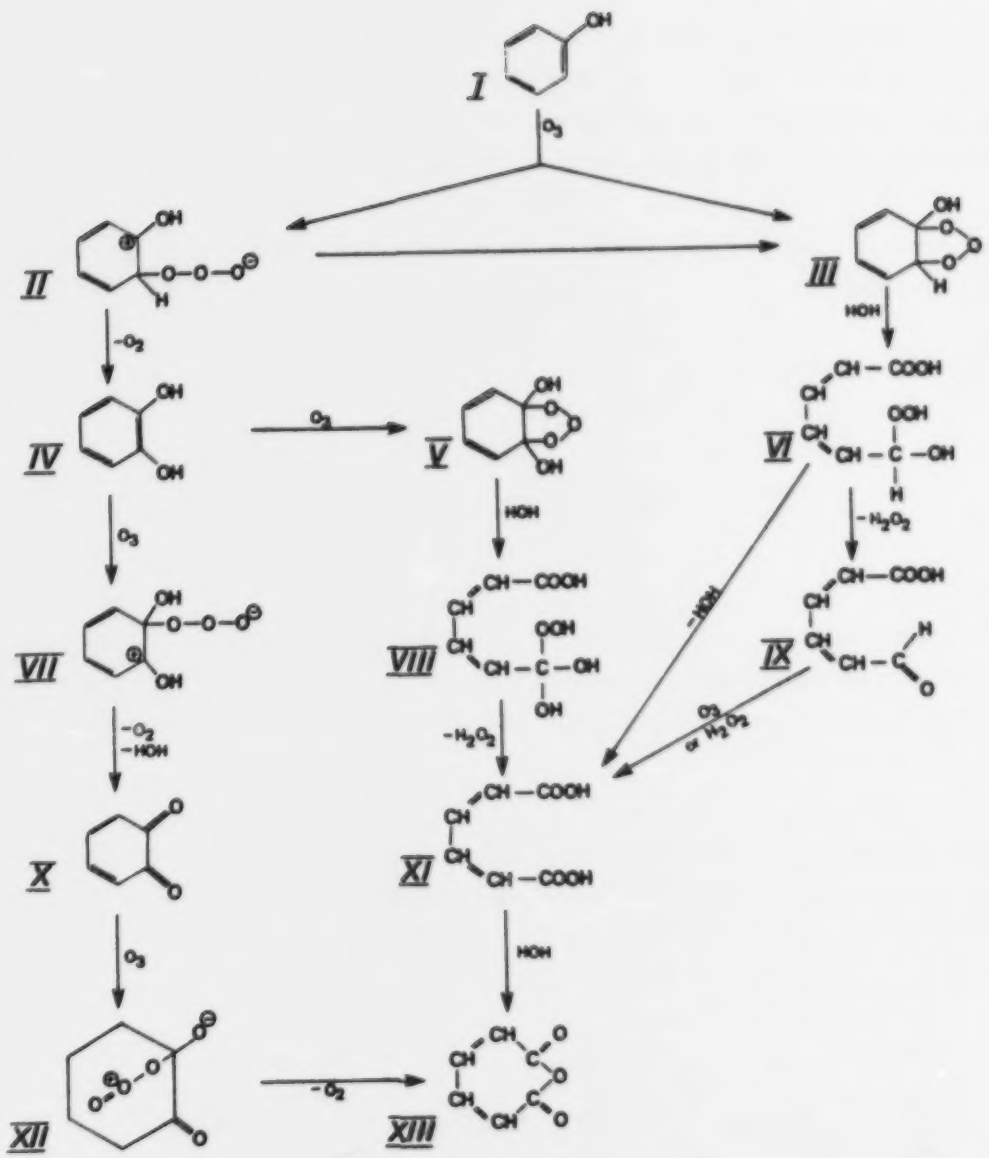
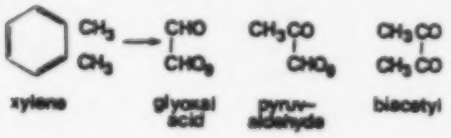


FIGURE 3.6-1 Oxidation of phenol by ozone in aqueous solution according to Eisenhauer (1971)

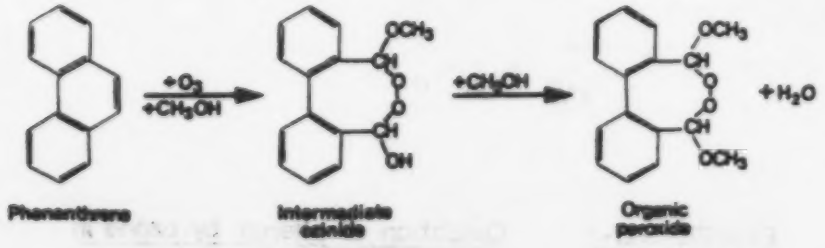
reaction products are not bioaccumulated (Korolev 1973). The stable reaction product, muconic acid, is readily decomposed biologically. The initial reaction is independent of pH but as the oxidation proceeds a higher pH is preferred. According to Soviet researchers, optimum conditions are promoted by lime additon and the end products are calcium oxylate and calcium carbonate (Kandzas and Molina 1972).

Another aromatic compound, xylene is oxidized to give a mixture of glyoxal acid, pyruvaldehyde and biacetyl.



The proportions of these compounds in the mixture indicate that the six bonds of the ring are attached in an equivalent manner and that the methyl groups produce a stearic effect. Catalysts such as boron trifluoride and aluminum chloride accelerate the reaction (Rickel et al. 1960).

Peroxides are formed by the action of ozone on certain condensed-ring compounds. Phenanthrene, for example, reacts with ozone in the following way:



A great deal of information is available in the literature concening the reaction mechnanisms of ozone with organic compounds. Good summaries are available (Othmer, 1961, Horvath et al. 1985) and this information will not be further discussed in this report. The important point is that numerous reaction products are possible and each treatment approach requires separate study. In some cases, the reaction products are reportedly as toxic as or more toxic than ozone. Such is the case in the treatment of malathion and parathion with ozone (Laplanche et al. 1972). Chlorinated pesticides (i.e. DDT, aldrin, lindane, etc.) can also be effectively treated by ozone but the toxicity of the end products was not evaluated (Gardiner and Montgomery 1968; Boucher et al. 1967). Bauer (1972) reports some cases of toxic intermediates.

3.6.2 Toxicity

Wedemeyer, Nelson and Yasutake (1979) recommend that dissolved ozone should be reduced to at least 2 mg/L to minimize adverse impacts on salmonids in receiving waters. They determined the lethal threshhold level of ozone to be about 8 mg/L with death apparently resulting from massive destruction of the gill lamellar epithelium together with a severe hydromineral imbalance. At 5 mg/L ozone, gill pathological changes were noted as well as reduced feeding behaviour in "partial chronic" (3-month) testing. Approximately 2 mg/L ozone caused no significant biological damage. Further results of toxicity tests (Asburg and Coler 1980) indicate that eggs of most species tested will be protected during short exposures (20 minutes) to moderate residuals (L1 mg/L) of ozone in natural water. Larvae of species tested were killed by virtually any measurable residual at even very short exposures.

From an aquatic toxicity perspective, then, the application of ozone should take into account the life cycle of species which might be exposed as well as relatively low concentrations which could adversely affect fishes at other than the egg stage.

Insofar as the human physiological effects of ozone are concerned, inhalation causes a range of symptoms varying from its unpleasant smell to pulmonary edema or lethal poisoning; ozone primarily affects the lungs (Horvath et al. 1985). Lung capacity, for example, is reduced to about 58% of its original value when air is inhaled that contains 6 ppm ozone.

Certain plants can degrade over time in the presence of ozone at exposure levels of 0.02 ppm for 4-8 hours or 0.05 ppm for 1-2 hours (Horvath et al. 1985). Plants show wide differences in their sensitivity to ozone with the more sensitive species displaying damage on leaves, often flecking, as ozone decomposes chlorophyll.

3.6.3 Field Use

Ozone generators have been developed to an advanced state largely for use in water treatment plants. Their utilization for the in-situ amelioration of chemical spills, however, appears to be somewhat questionable, depending upon the circumstances. A unit employing a corona discharge that produces of the order of kilograms of ozone per hour could cost hundreds of thousands of dollars and require a substantial sized power source at 4-6,000 megaHz and 30,000 volts (Dobie 1985). This could present severe limitations particularly as regards the mobility of a self-contained ozone treatment system.

Additionally, since the ozone stream produced would be limited to a pressure of less than 30 psi, it would be incompatible with injection systems requiring 100 psi pressure or greater. Ozone use would than be restricted to its direct injection in shallow water. A booster compressor would not be of assistance since ozone is unstable at elevated pressures and temperatures and would decompose to simple oxygen (Robinson 1979). Ozone application in the field is therefore in doubt when direct injection is considered from a portable generator.

The wide range of possible by-products and associated toxicities is another factor that has to be considered before field use can be planned. This would entail review of spills on a case-by-case basis to determine if a significant decrease in environmental

impact might result upon ozone treatment. In incidents where a lower rate of injection could be set up to treat a contained spill over time, then the approach could have considerable merit due to the strong oxidizing capability of ozone. An alternative would be to consider the utilization of an ozone treatment system to which the contaminant could be pumped for chemical conversion. Such waste processing equipment could cost of the order of $25,000 for a machine that produces ozone at the rate of 1 kg/h or $60-$70,000 for a somewhat larger system (Bell 1985).

3.6.4 Laboratory Investigations

Experiments were carried out to determine the effectiveness of ozone oxidation to reduce concentrations of three organic contaminants:

- phenol - due to its toxicity and prevalence of commercial use, information in the literature on which to base the experiment and to allow comparisons with H_2O_2 experiments (see Section 3.5.4).
- formalehyde - toxic organic chemical and widely used commercially.
- ethylene dichloride - due to a recent spill in Fort Langley, B.C.

Experimental Approach - The ozonation experiments were carried out using a Griffin Technics Inc. laboratory-scale water-cooled ozone generator. The samples were placed in a 2-litre contact chamber (one metre high, approximately 6 cm in diameter). Ozone was purged through the sample at a rate of 11.5 grams/hour. The ozone was 3.25% by weight of the total gas flow through the sample.

Samples were removed at specific intervals and analysed for pH, ozone concentration and for the compound under investigation. The starting concentrations of the contaminants investigated were:

phenol	1,000 mg/L
formaldehyde	1,210 mg/L
ethylene dichloride	19,000 mg/L

The analysis methods used are summarized below.

phenol - 4 amino/antipyrene method (Standard Methods, 1981)
formaldehyde - chromotropic acid method (WCB, 1984)
ethylene dichloride - head space with gas chromatography (FID detection)
ozone - Hach Kit - colorimetric method.

Results and Discussion - The results of the phenol ozonation experiments are summarized in Table 3.6-1. Two experiments were carried out, one at a neutral starting pH and one at an alkaline starting pH. The alkaline pH dramatically increased phenol oxidation as initially reported by Kandzas and Mokina (1972). At the higher pH, the ozone reaction created a very dark colour, probably due to the formation of a coloured intermediate. This darkness faded during subsequent ozonation. At 19 minutes the final solution was "straw" coloured. The pH dropped very quickly in both solutions, probably due to the formation of organic acid intermediates and the final reaction product (i.e. muconic acid - see Table 3.6-1 below).

Table 3.6-1. Ozonaton of Phenol.

Sample Description	Time of Ozonation (min)	pH	Phenol Concentration (mg/L)
Phenol Solution - pH adjusted at time = 0 to 7.0	0	7.0	1,100
	7	3.05	580
	12	2.70	17.5
	18	2.50	0.6
Phenol Solution - pH adjusted at time = 0 to 11.0.	0	11.0	1,050
	8	6.5	147
Additional lime added at 13 min.	13	5.7	2.0
	19	6.0	L0.2

L = less than (not detected)

NOTE: ozone residuals ranged from 0.2 - 0.5 ppm immediately after removal from chamber.

The results obtained from ozonation of formaldehyde are summarized in Table 3.6-2 below.

Table 3.6-2. Ozonation of Formaldehyde.

Sample Description	Time of Ozonation (min)	pH	Phenol Concentration
Formaldehyde - lime added to pH of 8.5	0	8.5	1,100
	7	5.7	116
	12	5.05	90
	19	5.00	Interference

Again a dramatic drop in formaldehyde concentration was observed after 7 minutes. Unfortunately, it was difficult to determine the final concentration of formaldehyde due to an interference problem with the analysis possibly due to the formation of an intermediate. Insufficient time was available to resolve this problem. As shown with the phenol experiments, pH control can have a dramatic effect on ozonation efficiency. Additional experiments should be carried out to determine optimum conditions for formaldehyde oxidation.

The results of ozonation of ethelyene dichloride are shown in Table 3.6-3 below.

Table 3.6-3. Ozonation of Ethylene Dichloride.

Sample Description	Time of Ozonation (min)	pH	Ethylene Dichloride Concentration (mg/L)
Ethylene Dichloride in water, no pH control	0	5.80	19,000
	7	5.22	13,500
	12	5.30	4,000
	19	5.40	5,070

A concentration of 19,000 mg/L was selected on the basis of experience by ASL on a recent spill in Fort Langley, B.C. Groundwater containing concentrations of this order or higher were frequently encountered.

Ozonation did not significantly reduce the concentration of ethylene dichloride and the reductions observed could be due to sparging rather than actual oxidation. Another experiment was conducted whereby a two-litre sample of water containing ethylene dichloride at 10,000 mg/L was aerated and a comparable reduction in concentration was observed.

These experiments demonstrate that ethylene dichloride is probably resistant to oxidation by ozone. Further experimental work would be required to confirm this preliminary finding.

3.6.5 Summary

Ozone is a very powerful oxidizer that produces oxygen when it reacts with inorganic compounds. It will combine with organic substances to give numerous by-products and reaction products which may or may not be toxic, depending upon the nature of the compound to which it is applied. Ozone treatment would have to be considered for each specific situation as regards the potential merit of its use. Excess ozone, various catalysts, and ambient conditions all can dictate the rate at which the reaction proceeds as well as its degree of completion.

Insofar as the toxicity of ozone itself is concerned, it could conceivably cause lethal poisoning to humans although this should generally be unlikely because its injection can be easily controlled and inhalation can be avoided. Fish larvae can, however, be killed by any measurable amount of residual ozone, whereas eggs remain protected for short exposures; a lethal threshold level of 8ug/L has been noted for salmonids, which is relatively high.

It is questionable whether or not a portable ozone generator could be effectively used for in-situ treatment of spills into flowing waterways. High cost and power requirements, lack of mobility, and injection problems could all possibly contribute to its rejection as a practical cleanup approach. However, where ozone can be injected into a isolated contaminant over time or in the event that the released toxin can be pumped to a portable ozone treatment system, its utilization could be considered. Inorganics would be particularly amenable to such processing.

The laboratory experiments conducted via this study served to confirm the effectiveness of ozone on selected contaminants such as phenol and formaldehyde. The work also demonstrated the importance of variables such as pH (a minimum of 9, optimum level of 12 was determined for cyanide treatment); the need for excess O_3 for some toxins (cyanide will then break down to give CO_2 and N_2); the possible formation of side reactions (ozonides form when O_3 reacts with organics); and its inappliability to some compounds such as ethylene dichloride.

3.7 Other Oxidizing Agents

The previous two chapters (3.5 and 3.6) dealt with two strong oxidizing agents - hydrogen peroxide and ozone. This section discusses other oxidizing agents that could be considered for spill control although many are utilized in chemical processing plants (an area to be excluded in this study). A brief review of oxidizers is presented, however, because of their inclusion in many spill control handbooks.

Oxidizing agents vary in strength as illustrated by the following half reactions arranged in order of decreasing oxidation potential.

Half Reaction	Oxidation Potential (E.) (Volts)
$F_2 + 2H^+ 2e^- \longrightarrow 2HF$	3.06
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$	1.77
$MnO_4 + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$	1.695
$HOCl + H^+ + 2e^- \longrightarrow Cl^- + H_2O$	1.49
$Cl_2 + 2e^- \longrightarrow 2\ Cl^-$	1.359
$Br_2 + 2e^- \longrightarrow 2\ Br^-$	1.09
$Cr_2O_7^{=} + 14H^{=} + 6e^- \longrightarrow 2\ Cr^{+++} + 7H_2O$	1.33
$I_2 + 2e^- \longrightarrow 2I^-$	0.54
$O_2 + 2H^+ \longrightarrow 2\ OH$	0.40

There are many good oxidizing agents for laboratory use but few offer convenient commerical utilization potential.

3.7.1 Chlorine

The most commonly employed oxidizing agent for use in wastewater treatment is chlorine.

i.e.	Chlorine Gas	Cl_2
	Sodium hypochlorite (bleach)	NaOCl
	Calcium hypochlorite (dry bleach)	$Ca(OCl)_2$
	Chlorine dioxide	ClO_2

Chlorine gas is commonly employed as a disinfectant in large water and sewage treatment plants. Sodium hypochlorite and calcium hypochlorite are finding increasing use especially in smaller water and wastewater plants due to safety considerations. Chlorine gas and the hypochlorites react in water to form hypochlorous acid.

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$$
$$NaOCl + H_2O \longrightarrow HOCl + Na^+ OH^-$$

The hypochlorous acid ionizes as shown by an equilibrium reaction.

$$HOCl \longrightarrow H^+ + OCl^-$$

The quantity of HOCl and OCl^- that is present in water is called the free available chlorine. At a pH of 7.5 and a temperature of 25°C the free available chlorine is half OCl^- and half HOCl (Johnson 1975). At lower pH more HOCl is present. HOCl is 40 - 80 times more efficient than OCl^- as a disinfectant.

Chlorination is used to oxidize many toxic substances, the most common of which is the alkaline chlorination of cyanide. The destruction is believed to proceed according to the following equations (Kiang and Metry 1982):

$$NaCN + Cl_2 \longrightarrow CNCl + NaCl$$
$$CNCl + 2NaOH \longrightarrow NaCNO + NaCl + 2H_2O$$
$$2NaCNO + 4NaOH + 3Cl_2 \longrightarrow 6NaCl + 2CO_2 + N_2 + 2H_2O$$

While chlorine is an effective oxidant, its use in spill control would be limited because of the toxicity of the chlorine residuals. Furthermore, additional toxic substances can be formed by the reaction of chlorine with other chemicals (i.e. chloramines from reaction with nitrogen; cyanogen chloride in the above reaction with cyanide; and trihalomethanes from reaction with certain organic compounds).

The toxicity of chlorine and related compounds is very well documented. It is known, for example, that the inhalation of chlorine can lead to pulmonary edema while its ingestion can ultimately result in convulsions, coma and death. Chlorine is considered to be highly toxic by inhalation (Environment Canada 1984):

TLV (inhalation) = 1 ppm; 3 mg/m^3
Short-term Inhalation Limits = 3 ppm; 9 mg/m^3 (15 min.)
LC_{50}-inhalation (rat) = 293 ppm/1 hr

3.7.2 Potassium Permanganate

Potassium permanganate is also commercially used as an oxidant in wastewater treatment for compounds such as aldehydes, mercaptans, pesticides, organic sulfur compounds, phenols and unsaturated acids (Kiang and Metry 1982). It is considered a relatively powerful oxidizing agent. A reaction product in the use of permanganate is manganese dioxide (MnO_2) which is insoluble in water and is normally removed by filtration.

Oxidation by permanganate is an accepted method of cyanide removal.

$$2KMnO_4 + 3CN^- + H_2O \longrightarrow 3CNO^- + 2MnO_2 + 2OH^- + 2K^+$$

The reaction proceeds only to form cyanate, and hydroxide continuously evolves which keeps the reaction on the alkaline side (Kiang and Metry 1982). A pH of at least 11.0 is required for successful oxidation of cyanide.

Permanganate can also be used to oxidize phenol as shown in the following theoretical reaction:

$$3C_6H_5(OH) + 28KMnO_4 + 5H_2O \longrightarrow 18CO_2 + 28\ KOH + 28\ MnO_2$$

Spicher and Skrinde (1965) propose that the reaction mechanism involves first the production of quinone and then the rupture of the ring followed by the oxidation of the ring fragments, if sufficient oxidant is present. It would be important to take the reaction as far as possible to completion because quinone is considered more toxic than phenol itself.

Potassium permanganate is probably reasonably safe to use from an environmental standpoint. It is itself not extremely toxic and its final reaction product, MnO_2 is not water soluble.

Potassium permanganate is frequently used to disinfect fish tanks and its moderately low toxicity is illustrated by the following data (McKee and Wolf 1976):

Table 3.7-1. Toxicity of Potassium Permanganate.

Concentration in mg/L	Type of Water	Time of Exposure	Type of Fish
3.0			Bluegills
3.2	Tap	24-hour TLm	Fingerling catfish
4.0			Largemouth bass
5.0			Fathead minnows
5.2	U.S.mn.	24-hour TLm	Bluegill sunfish
5.4	U.S.mn.	48-hour TLm	Bluegill sunfish
6.25		24 hours	Trout
10	Hard	12-18 hours	Goldfish
11.8		8 hours	Young eels
12	Turbid	24 & 96-hour TLm	Mosquito-fish
22-62		30 minutes	Fish

The commercial use of potassium permanganate is limited because of its expense and because of the need for filtration of the reaction product. It could present aesthetics problems if used for in situ spill control. A potassium permanganate solution is highly coloured and could cause severe staining. The reaction product MnO_4 is a dark insoluble precipitate which may be difficult to recover.

3.7.3 Other Oxidizers

Chromic acid (CrO_3) and sodium persulfate are also good oxidizing agents but would be too expensive for field use. Furthermore, the use of chromium would not be desirable environmentally because of its known toxicity.

Potassium ferrate (K_2FeO_4) is another powerful oxidizing agent exceeded only by ozone, fluorine and a few oxyfluorine compounds (Miller 1975). It is used as a laboratory oxidant and due to its instability it is normally prepared as needed. It has been proposed for general use in wastewater treatment because of strong oxidizing properties and its low toxicity (Weber 1972). However, Weber further points out that the relatively low thermodynamic stability and high cost render the feasibility of using ferrate in this application questionable. Should these problems be solved by an efficient manufacturing process, this product could easily find increasing use as an oxidant in waste treatment. Its potential application to spills, however, still remains in doubt.

3.7.4 Summary

Of the oxidizing agents described above only potassium permanganate could perhaps be considered for potential use in spill control. Even this product may create problems from an aesthetic standpoint and it appears to offer no significant advantage over that of hydrogen peroxide. Generally, oxidizing agents may react violently in the presence of significant quantities of readily oxidizable organics and require pH adjustments to ensure efficiency of reaction (Environment Canada 1985).

3.8 Reducing Agents

Chemical reduction is employed in waste treatment primarily to lower the oxidation state of metals (mainly chromium) and to dechlorinate. The most commonly employed reducing agents are various base metals such as aluminum, zinc, and iron (usually ferrous sulfate); sulfur compounds such as SO_2 and sulfite; and alkali metal hydrides - usually borohydride.

3.8.1 Sulfur Compounds

The most common sulfur compounds used for chemical reduction are:

Sulfur dioxide	SO_2
Sodium bisulfite	$NaHSO_3$
Sodium sulfite	Na_2SO_3
Sodium metabisulfite	$Na_2S_2O_5$

Sulfur dioxide gas successively removes free chlorine, monochloramine, dichloramine, nitrogen trichloride, and poly-n-chlor compounds. When sulfur dioxide is added to wastewater containing chlorine, the following reactions occur (Metcalf and Eddie 1979).

$$SO_2 + H_2O \longrightarrow HSO_3^- + H^+$$
$$HOCl + HSO_3^- \longrightarrow Cl^- + SO_4^= + 2H^+$$
$$SO_2 + HOCl + H_2O \longrightarrow Cl^- + SO_4^= + 3H^+$$

Reaction with chloramines:

$$SO_2 + H_2O \longrightarrow HSO_3^- + H^+$$
$$NH_2Cl + HSO_3^- + H_2O \longrightarrow Cl^- + SO_4^= + NH_4^+ + H^+$$
$$SO_2 + NH_2Cl + 2H_2O \longrightarrow Cl^- + SO_4^= + NH_4^= + 2H^+$$

For the overall reaction between sulfur dioxide and chlorine, the stoichiometric weight ratio of sulfur dioxide to chlorine is 0.9:1. In practice, it has been found that about 1:1 will be required for dechlorination of chlorine residue (expressed as Cl_2). Because the reactions of sulfur dioxide with chlorine and chloramines are nearly

instantaneous, contact time is not usually a factor and contact chambers are not used, but rapid positive mixing at the point of application is an absolute requirement.

Dechlorination may be appropriate for a spill of hypochlorite (most likely sodium hypochlorite since this is a liquid). Sodium bisulfite (or sulfite or metabisulfite) would be used to reduce the hypochlorous acid and the same reactions would occur, i.e.:

$$NaOCl + H_2O \longrightarrow Na^+ + HOCl^- + OH^-$$
$$Na_2HSO_3 \longrightarrow 2Na^+ + HSO_3^-$$
$$HOCl + HSO_3 \longrightarrow Cl^- + SO_4^+ + 2H^+$$

Dramatic pH changes would be possible that result from insufficient use or overuse of sodium sulfite salts for dechlorination. A sodium hypochlorite spill would create caustic conditions which would be neutralized by the hydrogen ions produced from the dechlorination reaction. The stoichiometry of the reaction shows that neutrality would be achieved by the correct use of chemical quantities. However, at a spill site this may be difficult to achieve and it would be advisable to have neutralizing chemicals (acid and caustic) ready for use, if required.

Additional side reactions are not anticipated or would not be significant if they were to take place. Some ions naturally present in the environment may become reduced, but their initial concentrations would be low in relation to the hypochlorous acid and therefore significant quantities of sulfite would not be consumed.

While sulfur dioxide is highly toxic to humans, aquatic life and plant foliage (Environment Canada 1984), compounds such as sodium sulfite are usually far less toxic by ingestion. For example, 2600 ppm sodium sulfite solution is toxic to fish over 24 to 96 hour test periods. Death in humans can also result if sufficient quantities of sodium sulfite are taken internally. Inhalation and skin contact can cause minor irritations so that care must be taken to avoid intimate contact.

Similarily, sodium metabisulfite has been found to be moderately toxic. It is lethal to minnows at 75-80 mg/L in hard water at 17°C while sodium bisulfite is lethal to minnows at 80-85 mg/L in hard water at 18°C (McKee and Wolf 1976).

Sulfur dioxide and sulfites are used commercially to reduce hexavalent chromium which is toxic in the +6 (Cr VI) valence state but much less toxic in the +3 (CrIII) valence state i.e.:

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$2\,H_2CrO_4 + 3H_2SO_3 \longrightarrow Cr_2(SO_4)_3 + 5H_2O$$

or with metabisulfite

$$4H_2CrO_4 + 3Na_2S_2O_5 + 3H_2O + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6NaHSO_4 + 10\,H_2O$$

The chromium III is then neutralized by lime (1.1 kg of hydrated lime is required to neutralize 1 kg of reduced chromic acid).

$$Cr_2(SO_4)_3 + 3\,Ca(OH)_2 \longrightarrow 2\,Cr(OH)_3^{+} + 3\,CaSO_4$$

Hexavalent chromium can be reduced in wastewaters to the range of 0.7 - 1 mg/L by this process of reduction followed by precipitation. pH is an important consideration in chromium reduction and must be maintained between 2 and 3. Such a low pH is not desirable for in-situ spill treatment and this limits the usefulness of this method for spill control.

3.8.2 Ferrous Sulfate

Another relatively common reducing agent is ferrous sulfate, e.g. for chlorine:

$$6FeSO_4 + 3\,Cl_2 \longrightarrow 2\,FeCl_3 + Fe_2(SO_4)_3^{+}$$

e.g. for chromic acid

$$6\ FeSO_4 + 2\ H_2CrO_4 + 7H_2O + 6H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3\ Fe_2(SO_4) + 50H_2O$$

In the latter reaction a pH of 2 - 3 is required which, as discussed above, is not desirable for in-situ spill control. A second problem with ferrous sulfate use is the production of iron sludge (i.e. $FeCl_3$ and $Fe(OH)_3$) as a reaction product. This limits its use in waste treatment plants and would not be desirable for in-situ use.

3.8.3 Other Reducing Agents

In specific cases sodium borohydride has been used as a reducing agent — to control mercury and lead contamination. In a reduction/precipitation process which has been used commercially, a caustic solution of sodium borohydride ($NaBH_4$) is mixed with mercury containing wastewater (Kiang and Metry 1982). The ionic mercury is reduced to metallic mercury which precipitates out of solution.

$$4Hg^{++} + BH_4^- + 80H^- \longrightarrow 4Hg + B(OH)_4^- + 4H_2O$$

In theory 1 kg of sodium borohydride can reduce 21 lb of mercury; however, in practice the yield is closer to 10 lb. Lead can be similarly reduced by borohydride at a pH of 8 to 11.

It is felt this reaction is a batch process and its use for in-situ spill control would be limited and only applicable if the spill were contained.

Other base metals can also be considered as chemical reducing agents, i.e. powdered waste iron, aluminum, zinc, but little is reported in the literature concerning their use. In general, reduction is most efficient when controlled in wastewater treatment systems (Environment Canada 1985).

3.9 Carbonate Precipitation

3.9.1 Chemistry

It is well known that the toxicity of heavy metals is significantly reduced in hard waters. This is due to formation of carbonate salts which are normally insoluble in water. Carbonate precipitation, then, should provide an effective approach for treating heavy metal spills.

Most carbonate salts are insoluble in water. Calcium carbonate (or chalk) is the most common carbonate salt and requires an acidic solution to achieve dissolution. Additon of acid produces carbon dioxide gas and forms a soluble salt of calcium.

$$\text{i.e. } 2HCl + CaCO_3 \longrightarrow CaCl_2 + H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2$$

Robinson (1979) discusses carbonate precipitation of metals but only refers to the use of sodium bicarbonate for the treatment of cadmium, iron and zinc and not the other toxic heavy metals. Most bicarbonate salts are relatively water soluble.

It seems more reasonable to use sodium carbonate (Na_2C0_3) as a source of soluble carbonate ions. Sodium carbonate is soluble in water (1 part in 3.5 parts water at 20°C) and is readily available. The carbonate ion would rapidly form with dissolved metal ions to combine carbonate precipitates.

$$\text{i.e. } CuSO_4 + Na_2CO_3 \longrightarrow CuCO_3 + Na_2SO_4$$

The precipitation reaction is straightforward and the only side reaction that would occur would be the formation of carbonates with other dissolved metals in the receiving water. Dissolved calcium and magnesium are present in varying concentrations in most surface and groundwaters and these cations would combine with carbonate to form calcium carbonate and magnesium carbonate. Therefore, an excess of sodium carbonate would need to be added.

One possible disadvantage of using sodium carbonate is its high pH (pH of a 1% solution is over 11.0). This, however, may be an advantage in that many heavy metal spills create acidic conditions and the addition of sodium carbonate may tend to neutralize the acidity and complex the dissolved metal. This was further investigated in the laboratory (see Section 3.10.4).

3.9.2 Toxicity

The toxicity factor associated with sodium carbonate is generally low for humans and drinking water with concentrations of 360-500 mg/L has been considered "wholesome and safe" (McKee and Wolf 1976). However, medium tolerance limits (TLm) for fish exposed to sodium carbonate for 96 hours can vary from 300 mg/L for sunfish to 1,200 mg/L for mosquito-fish. More sensitive species, such as chinook salmon, succumb in 120 hours when concentrations are as low as 68 mg/L (McKee and Wolf 1976). Ingestion by humans would similarly be fatal if large amounts were taken internally. This is due to the corrosive nature of sodium carbonate, specifically to the gastrointestinal tract (Environment Canada 1984).

Overall, then, the in-situ application of sodium carbonate for spill treatment would have to be strictly controlled so that excessive concentrations did not result. While irritation to the upper respiratory system and skin can also occur, the otherwise relatively inocuous nature of sodium carbonate to humans at low concentrations in water belies its potential effects on aquatic organisms at the same levels.

3.9.3 Field Use

Sodium carbonate is highly soluble and, based on this aspect, could theoretically be applied to ameliorate the effects of spills in waterways. Over-addition would have to be avoided because of the high pH (12 or more) that may be attained (Robinson 1979) and associated toxicities. Broadcasting the dry format or pumping a liquid concentrate could be readily accomplished if the circumstances of the incident allowed such response action to be taken. Various grades and purities in both liquid and powder form can be purchased.

A main concern as regards the field use of sodium carbonate is the potential need to add it in excess due to the precipitation of calcium carbonate and magnesium carbonate (from dissolved calcium and magnesium cations). Critical values of pH could result which might not significantly reduce the toxicological risk of the original contaminant. The current laboratory studies demonstrated exacting needs in determining the correct amount of treating agent which must be added to precipitate metals. This may not always be possible for in-situ spill treatment. The stability of the sodium carbonate-metal complex is also somewhat in question particularly in situations where the pH returns to background levels over time. Utilization of sodium carbonate as an in-situ treating agent is therefore likely limited to special cases where localized or isolated contamination has occurred.

3.9.4 Laboratory Investigations

A number of experiments were carried out to examine the effectiveness of sodium carbonate to precipitate dissolved copper from solution.

Experimental Approach - First, titrations were carred out to demonstrate the effect of sodium carbonate addition on pH. One litre of distilled water and one litre of a 5 ppm copper solution (prepared with copper sulfate) were titrated with sodium carbonate.

To establish an equivalence point, a series of 5 ppm copper solutions (one litre volume) were treated with increasing quantities of sodium carbonate. Aliquots were removed, filtered through a 0.45 micron membrane and analysed for copper by atomic absorption spectrophotometry.

The settling characteristics of the copper carbonate precipitate were tested by carrying out a settling experiment in a one-litre settling cone. One litre of copper sulfate (5 ppm Cu^{++}) was treated with excess Na_2CO_3 (2.5 mg). Aliquots were removed at frequent intervals and analysed for dissolved copper.

The effect of pH, temperature, water hardness and suspended sediments was also examined.

Results and Discussion

The results of the titration experiments are presented in Figure 3.10-1. To reach a pH of 8.5 in one litre of distilled water 15 mg of sodium carbonate were required. One litre of 5 ppm copper sulfate solution required 28 mg of sodium carbonate to attain a pH of 8.5. An overuse of sodium carbonate could produce a pH slightly over 9.0. The pH guidelines for high protection freshwater organisms is pH 6.0 to 9.0 (Environmental Canada, 1972; EPA, 1976).

A significant reduction in copper concentration was obtained by the addition of 2.5 mg of sodium carbonate (to one litre of 5 ppm Cu^{++}) which is more than twice the theoretical requirement based on the stochiometry (Fig. 3.10-2). Further experimentation demonstrated that pH is critical. At the stochiometric equivalence point, the pH was only 5.7 and the copper was reduced to 3.3 mg/L. In a separate experiment, the pH was raised to 7.0, and the dissolved copper concentration was drastically reduced to 0.31 mg/L.

This experiment demonstrates the need to add excess sodium carbonate to control copper concentrations. A weight ratio of 0.5-to-1 part sodium carbonate to 1 part Cu^{++} would adequately reduce the free copper concentration without adversely affecting pH.

A settling experiment was carried out and aliquots from the mid-point of a settling cone were removed and analysed for total and dissolved copper. The results obtained are presented in Table 3.9-1 below.

Table 3.9-1. Settling Rate of Copper Carbonate Precipitate.

Time	Copper Concentration (mg/L)	
	Total Cu^{++}	Dissolved Cu^{++}
-5 (before Na_2CO_3 addition)	5.10	5.10
0 (Na_2CO_3 added)	5.10	0.25
5 min	4.81	0.11
10 min	4.71	0.10
15 min	4.71	0.08
20 min	4.68	0.06
30 min	4.61	0.06
60 min	4.38	0.05
90 min	4.11	0.06
120 min	4.16	0.05

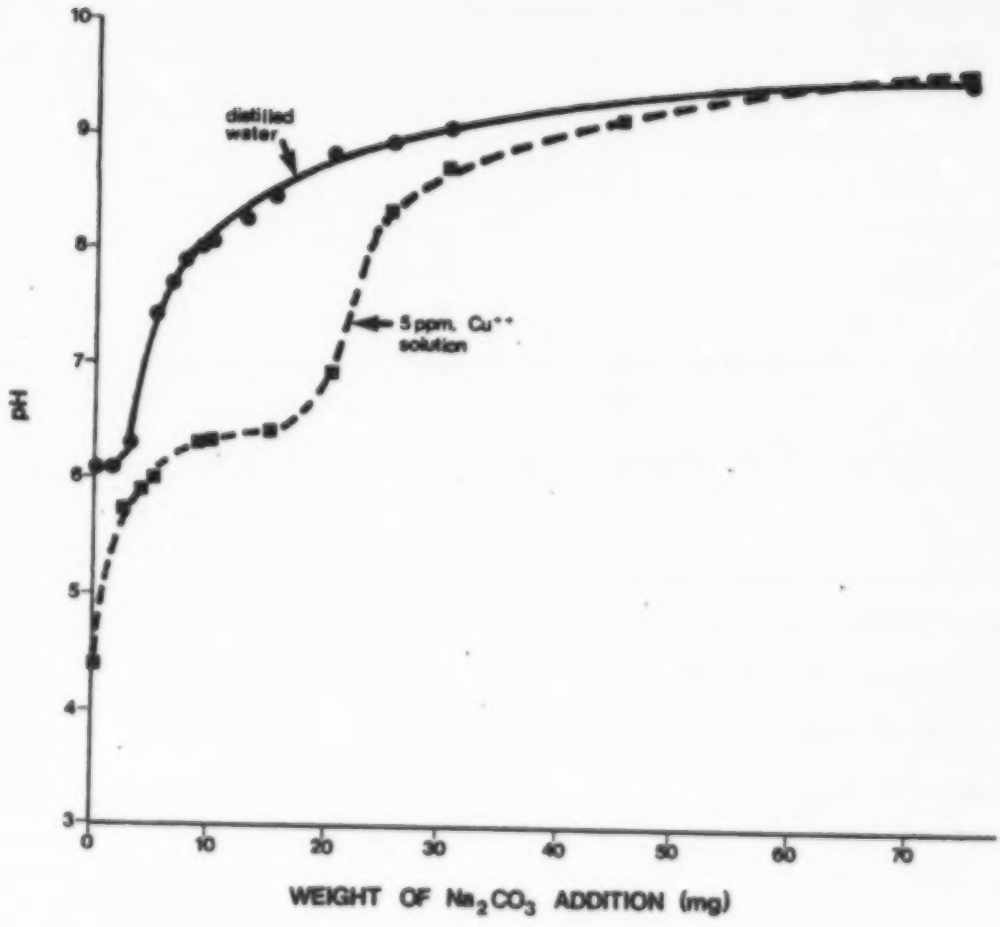


FIGURE 3.10-1 Titration curves with sodium carbonate added to one litre of distilled water and one litre of 5ppm. Cu^{++} solution (prepared with copper sulphate $CuSO_4 \cdot 5H_2O$)

These results demonstrate that, while the copper carbonate precipitate is rapidly formed (i.e. low dissolved copper concentrations), it does not settle adequately (high total copper concentrations). Thus, in utilizing sodium carbonate to treat a copper spill, it is probable that the precipitate would remain suspended in the aquatic environment and eventually become diluted over time.

This brought into question the stability of the complex with changes in pH. Further experiments were carried out to demonstrate whether or not the copper carbonate precipitate would partially re-dissolve if the pH was lowered using dilute sulfuric acid). The results obtained are shown below.

Table 3.9-2. Stability of Copper Carbonate Precipitate at Lower pH.

pH Value	Copper Concentration (mg/L)	
	Total Cu^{++}	Dissolved Cu^{++}
Before Carbonate addition pH = 3.8	5.00	5.00
After Carbonate addition pH = 8.1	5.05	0.10
ph adjusted to 6.50	5.01	0.90
pH adjusted to 5.90	5.03	2.06

Additional experiments were then carried out to determine the effects of temperature, water hardness and suspended sediments on the precipitate formation. The approach taken for these tests is similar to that taken for EDTA (Section 3.1.4). These three variables did not affect the precipitate formation. In fact, the free copper concentration was somewhat lower (see Table 3.9-3 below) than in the control test.

Table 3.9-3. Effect of Other Variables on Carbonate Precipitation.

Test Condition	Copper Concentration (mg/L)	
	Dissolved Cu^{++}	pH
1. Control Test - One litre 5 ppm Cu^{++} in distilled water, treated with 2.5 mg $NaCO_3$	0.12	8.1
2. Water hardness x 100 mg/L as $CaCO_3$	0.09	8.2
3. Temperature of 4°C	0.08	7.9
4. Suspended sediment (4,000 ppm)	0.08	7.9

3.10 Other Precipitating Agents

The previous section dealt with one chemical precipitating agent (carbonate) as a means of reducing free heavy metal concentrations. This section deals with other precipitants that may be considered for spill control.

Precipitation or clarification is a very common means of wastewater treatment. In treatment plants, a coagulant is first added, the most common being aluminum salts (alum), lime, iron salts and organic polyelectrolytes. In most cases, these chemicals form immediate precipitates on their own and the precipitation reaction involves other insoluble materials.

i.e.

$$Al_2(SO_4)_3 + 6\,HCO_3 \longrightarrow 2\,Al(OH)_3 + 3SO_4^{=} + 6CO_2$$

(alum) (bicarbonate) (alum floc)

The alum floc thus formed is gelatinous and settles reasonable quickly providing general clarification. Flocculation aids (usually polyelectrolytes) are then added to hasten settling or increase filtration efficiency. This type of clarification is mainly designed to control suspended solids in wastewater. As it is standard wastewater treatment technology, a great deal of information is available in the literature so that this subject will not be covered further in this report. A good summary is provided by Culp and Culp (1971).

Several precipitants were suggested by Robinson (1979) for possible use in spill control. Some of these would not be acceptable. Sulfide was one suggestion. It will form precipitates with most metals.

i.e.

$$Na_2S + CuSO_4 \longrightarrow CuS + 2\,Na^+ + SO_4^=$$

Sulfide, however is very toxic to fish. It is lethal to salmonid fish, in general, as well as to coho and chinook salmon, specifically, at concentrations of 1.8 to 3.5 mg/L (McKee and Wolf 1976). Fish avoidance of sodium sulfide solutions at 3.1 to 39.0 mg/L has been noted. When added to water, dissociated sulfide ions can react to form HS^- or H_2S depending upon the pH. This leads to further increases in toxicity particularly as pH decreases from 9 to 6 (McKee and Wolf 1976).

For this reason sulfide should not be considered for chemical precipitation.

Another possible precipitating agent is oxalate but again due to its toxicity, missapplication could have adverse effects. Many oxalates dissociate readily to result in an increase in pH. This could be sensitive to many life forms in receiving waters. McKee and Wolf (1976) report median tolerance limits (TLm) of 1,350 mg/L of sodium oxalate for mosquito-fish in 24 to 96 hour tests. They also note that 214 mg/L of sodium oxalate immobilized Daphnia magna. Robinson (1979) also briefly remarks upon the toxicity of the oxalate ion. Oxalate is clearly not favoured for use as a spill agent.

Hydroxide precipitation is by far the most common method of precipitating heavy metals. Lime ($Ca[OH]_2$) is the normal source of hydroxide and there is a great deal of information in the literature concerning lime treatment to precipitate metals (Patterson 1975) which will not be detailed here. The main problem in using lime for in-situ spill control is the requirement for a high pH. Usually a pH of 10 or more is required for effective precipitation. Such a pH is above water quality guidelines. Furthermore, because most freshwater bodies are neutral or alkaline there is a distinct possibility for redissolution of the precipitate as was demonstrated for the carbonate precipitate in Section 3.9.4.

Phosphate is also a possible precipitating agent and Robinson (1979) recommended dibasic sodium phosphate (Na_2HPO_4) as the most appropriate choice for precipitating divalent heavy metals. The reaction would be as follows:

$$Na_2HPO_4 \longrightarrow 2Na^+ + H^+ + PO_4^=$$

$$3Cu^{++} + 2PO_4^= \longrightarrow Cu_3(PO_4)_2$$

3.10.1 Laboratory Investigation - Phosphate Precipitation

On the basis of a recommendation by Robinson (1979) a series of experiments were conducted to assess the use of dibasic sodium phosphate to precipitate copper from solution.

Experimental Approach - A solution of copper sulfate (20 ppm Cu^{++}) was treated with increasing concentrations of dibasic sodium phosphate. The resulting solution was then filtered within 5 minutes and the filtrate was analysed for free copper by atomic absorption spectrophotometry.

Results and Discussion - The results obtained are given in Table 3.10-1. The results indicate a very critical dependence on pH; redissolution of the precipitate was evident as the pH increased beyond 7.1.

The precipitate formed was very fine and, like the copper carbonate precipitate. did not readily settle. A longer reaction time did not decrease the copper concentration. Suspended solids, low temperature and increased water hardness did not affect the results.

These experimental results indicate that dibasic sodium phosphate could be an effective precipitant. However, by comparison,the final dissolved copper results were higher than those obtained after carbonate precipitation (see Section 3.9.4). Furthermore, the critical dependence on pH control would restrict its usefulness in a field situation. Further work would be required to more fully document the pH effect.

Table 3.10-1. Results of Phosphate Precipitation.

Amount of 0.05M Na_2HPO_4 added to 1 litre of Cu Solution	pH	Dissolved Cu^{++}
0 ml	3.72	20.1
2 ml	4.78	3.93
4 ml	5.39	0.57
6 ml	6.11	0.43
8 ml	7.13	0.35
10 ml	7.35	1.00
15 ml	7.44	3.23
20 ml	7.56	4.02
50 ml	8.00	4.35
Additional Experiments		
6 ml, 4°C	6.78	0.55
6 ml, hard water (100 ppm $CaCO_3$)	7.10	0.50
6 ml, 4,000 ppm suspended solids	6.55	0.41
6 ml, 20 minute reaction time	6.53	0.59

3.11 Smectite Clay

Clay is defined as a widely distributed, colloidal, lusterless earthy substance, primarily composed of broken down igneous and metamorphic rocks. Clay is rich in feldspars (aluminum silicates) with crystalline grains less than 0.002 mm in diameter. Because of their size, clay particles expose a large surface area to the external environment. This combined with chemical reactivity make clay particles highly efficient in adsorbing and binding metal ions and many organic molecules.

Smectites are a subclass of clay minerals which have found increasing recognition as natural catalysts and binding agents. The majority of the research is new, and not extremely abundant. Nonetheless, it was felt worthwhile to devote a separate chapter to smectite clay because of its potential usefulness in treating chemical spills.

3.11.1 Physical Structure of Smectite

The name smectites refers to a group of phyllosilicates which include montmorillonite and related clay minerals (Mering 1975). All smectites have a lamellar structure consisting of sheets of silicone oxide either arranged in a tetrahedral or octahedral configuration. Smectites have two layers of tetrahedral sheets and one octrahedral sheet which is sandwiched between them. Because of the ratio of these two types of sheets, smectites are classified as a 2:1 type as shown in Figure 3.11-1. The common clay kaolinite, in contrast, is of the 1:1 type and has one octrahedral sheet and one tetrahedral sheet (Pinnavuia 1983). At the centres of the tetrahedral molecular arrangements normally a silicone atom is found but aluminum is also occasionally present. At the centres of the octrahedral configuration, aluminum, iron, or magnesium ions are often found as shown in Figure 3.11-1 (Pinnavuia 1983). In Wyoming montmorillonite clay, for example, the octrahedral sheets have Mg^{++} and Fe^{++} substituted for Al^{+++}. In the tetrahedral sites Al^{+++} displaces Si^{++++} resulting in an overall negative charge of about 0.66 per unit cell. The negative charge is balanced by adsorption of exchangeable cations on the sheet surface as well on the edges.

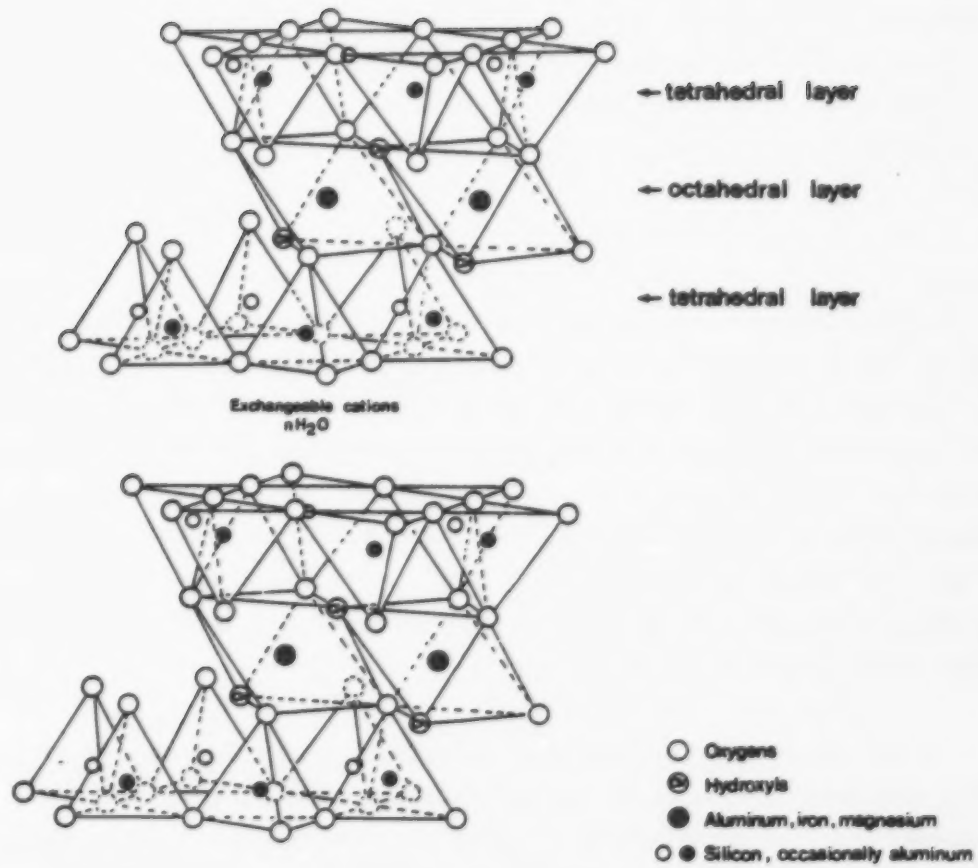


FIGURE 3.11-1 Configuration of smectites

When these composite layers of smectites come together as in a clay, the space between these layers can be filled with water molecules as well as exchangeable cations. Thus interlayer water is more ordered than liquid water, possibly having a structure similar to that of ice. Water thickness increases with the type of exchangeable ion that is present.

The exchangeability of cations of Group 1 and Group 2 of the periodic Table is related to the ionic radii, i.e., the smaller, more hydrated cations Li^+ and Na^+ are less strongly adsorbed than the larger monovalent cations of Group 1. Similar trends are observed with the divalent cations of Group 2. The following sequence of increasing adsorption strength is found (Cooper, 1976).

$$Li^+ < Na^+ < K^+ NH^+ < Rl < Cs < H^+ \text{ and } Mg^{++} < Ca^{++} < Sr^{++} < Ba^{++} < La^{++}$$

The swelling beyond a single molecular layer of intercalant such as water, is perhaps one of the most important properties of smectites regarding their catalytic properties. Li^+ and Na^+ exchange forms are highly susceptible to swelling by water. Increasing partial pressures of water will first produce a monolayer followed by an abrupt jump to a bilayer and this can continue until the silicone layers are completely dispersed or delaminated (McEwan and Wilson 1980). This will finally result in the formation of a gelatinous material at which stage the layers interact edge-to-face which has been called a "House of Cards" structure. A 2% suspension of Na^+ montmorillonite will result in complete dispersion or delamination.

Zinc was found to be adsorbed to Wyoming montmorillonite in excess of what is predicted from the value of its ion exchange capacity (92 Meq/100g). This excess adsorption of zinc (zinc fixation) occurred at the same time as anion adsorption. It was found that hydroxyl ions were most strongly adsorbed followed by Cl^- and NO_3^-. The zinc fixation is explained by irreversible incorporation of zinc atoms into the octohedral vacancies within the clay structure.

Potassium montmorillonite equilibrated with cupric acetate was found to adsorb Cu^{++} in excess of the K^{+} released. Similarly copper could be adsorbed at 22 Meq/100g in excess of the calcium ion exchange capacity (100 Meq/100g) and zinc could be adsorbed in excess of 4 Meq/100g. It was concluded that zinc and copper were adsorbed in excess by displacing protons from structural hydroxyl groups.

3.11.2 Application of Smectites in Water Treatment

Bentonite clay has been studied for its potential to adsorb trace concentrations of heavy metals from lime-treated mine waste waters (Cooper 1976). These waste waters, containing mostly salt solutions of calcium and sodium at a concentration of 10^{-2}N were found to exchange their heavy metals with montmorillonite with increasing pH (4 to 8). The site of adsorption was theorized to be at dissociated hydroxyl groups previously assumed unattractive to major cations. The adsorption efficiency in such waters was found to be Mn Fe(II) Zn Cu.

It was also observed that adsorption of zinc was much slower than that of copper, i.e. 100% adsorption of 100 micrograms of copper per litre in 10 minutes compared to 100 micrograms of zinc per litre which took 6 hours for a 60% completion. It appeared therefore that heavy metals can be adsorbed in excess of the alkali earth cations present, the extent of which is not exactly known or understood.

3.11.3 Catalytic Role of Smectites

The ability of smectites to swell and change the intramolecular layers is perhaps one of the most important properties regarding the catalytic properties of smectites. Many natural processes such as petroleum formation reactions, chemical transformations, and many of the reactions that have been related to chemical evolution take place on smectite clays. Many of these reactions require that neutral molecules are intercalated between the silicate layers of the smectites in question (Bothener and Motland 1977; Stul 1983). The adsorption of neutral molecules to smectites has been shown to exist and can

occur by several mechanisms. One of these is complex formation between the exchange cation and the intercalant such as the binding of pyridine to Cu^{++} exchanged forms of smectites (Pinnavuia 1983).

$$\overline{[Cu(H_2O)_x]^{++}} + \text{pyridine} \quad \overline{-H_2O\ [Cu(Py)_4]^{++}}$$

The horizontal bars signify the silicate layers. Similarly, ammonia binds as ammonium ions in Mg^{++} - montmorillonite.

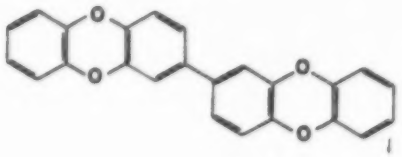
3.11.4 Phenol Degradation

Shawney et al. (1984) have shown that phenols have been capable of polymerization on dried smectite surfaces and that their products are strongly held by the clay and the soils. Under certain conditions, however, the adsorption and polymerization of phenols is prevented, resulting in the rapid movement of the phenol through the soil columns. One of these conditions occur when the soil column becomes saturated with the phenol. Another condition under which polymerization of phenols is prevented is in an anaerobic atmosphere. Lack of polymerization in aqueous solutions under nitrogen atmospheres has been observed in clays. Recent experiments involving o-methylphenol, o-chlorophenol and m-methylphenol have shown that adsorption and polymerization of these agents in air is much larger than under a nitrogen atmosphere. These observations provide a partial explanation as to why phenol transport could be facilitated in aerobic environments such as those found in land fill sites. The polymerization products include the dimers, trimers and tetramers of the parent phenol compound and their corresponding quinones. The degree of polymerization and its magnitude were highest for: Fe Al Ca Na - bound to the clay.

3.11.5 Dioxin Destruction

Wyoming bentonite clay has been used to study the catalytic destruction of dioxins. This catalytic destruction only occurs when copper ions have been introduced between the clay layers. This is readily achieved by washing the bentonite clay with a solution of a copper salt. The resulting clay is then freezed dried and ready for use. A boiling solution

of dioxin in hexane (69°C) produces dioxin radicals which then in turn produce dioxin polymers as shown below.



(DIOXIN POLYMER)

In this respect the detoxification process is achieved by the polymerization of the original agent of interest. Under normal conditions very high temperatures and strong acids are required to produce free radicals from dioxin molecules so that polymerization can take place with smectites. This is achieved at a very low temperature. Currently, Dow Chemical holds royalty-free licensing rights to the process of dioxin removal with smectite.

The claim is made that smectite clays are 20 times less expensive than the use of activated carbon for organic removal (Anonymous 1985).

3.11.6 Toxicity

Smectites are universally present in our environment and in this respect exposure to smectites as a dust or as a contaminant in water or food is unavoidable. No toxic effects with this type of exposure have ever been reported. Oral ingestion of smectites is often used to curb gastrointestinal problems. Smectites apparently delay the adsorption of basic drugs but not that of acidic drugs (Albengies et al. 1985; Droylefaix 1985). Studies have suggested that the presence of smectites in the GI tract may cause the polymerization of mucous by interacting closely with glycoproteins. This then improves the quality of the mucous that lines the GI tract, making it more capable of resisting the mechancial trauma present at these surfaces.

3.11.7 Summary

The information presented on smectite clays demonstrates the mechanisms by which they adsorb chemicals and behave as catalysts. The research is new especially with regard to waste treatment. It is therefore premature to speculate on the usefulness of these materials in spill control. However, because of their low cost, absence of toxic effects and apparent versatility (i.e. application to inorganics and organics) it is concluded that further investigations are definitely justified.

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APPENDIX I Environment Canada List of Priority Substances.

List of Priority Hazardous Materials For the
Environmental Emergency Branch
The 50 Highest Priority Chemicals
(In alphabetical Order)

Acetic Acid
Acetic Anhydride
Ammonia
Ammonium Nitrate
Ammonium Phosphates
Benzene
Butyraldehydes
Calcium Chloride
Calcium Oxide/Hydroxide
Carbon Dioxide
Chlorine
Cyclohexane
Ethylbenzene
Ethylene Dichloride (1,2-Dichloroethane)
Ethylene Glycol
Ethylene Oxide
Ethylene
Ferric Chloride
Formaldehyde
Hydrogen Chloride/Acid
Hydrogen Fluoride/Acid
Hydrogen Sulfide
Mercury
Methanol
Morpholine
Naphtha
Natural Gas
Nitric Acid
Phenol
Phosphoric Acid
Phosphorous
Potash (Potassium Chloride)
Propylene Oxide
Propylene
Sodium Chlorate
Sodium Chloride
Sodium Hydroxide
Sodium Hypochlorite
Sodium Sulfate
Styrene (Monomer)
Sulfur Dioxide
Sulfuric Acid (and Oleum)
Sulfur
Tetraethyl Lead
Toluene
Urea
Vinyl Chloride
Xylenes
Zinc Sulfate
2-Ethylhexanol

APPENDIX 1 - (Cont'd)

The Second Group of Priority Chemicals
(100 substances or groups)

Acetone
Acetylene
Acrylonitrile
Adipic Acid
Aluminum Chloride
Aluminum Hydroxide
Aluminum Sulfate
Aminocarb Pesticide (Matacil)
Ammonium Chloride
Ammonium Sulfate
Arsine
Barium Sulfate
Benzoic Acid
Borax
Boric Acid
Butanols
Butylene
Calcium Carbide
Calcium Carbonate
Calcium Hypochlorite
Calcium Phosphate
Caprolactam
Carbaryl
Carbofuran Pesticides
Carbon Disulfide
Carbon Tetrachloride
Chlordane
Chloroform
Copper Sulfate
Cresols
Dicamba
Dichlorobenzene
Dimethyl Ether
Dimethyl Terephthalate
Dinoseb
Diphenylmethane-4,4'-Diisocyanate
Ethanolamine
Ethanol
Ethylene Dibromide
Fenitrothion
Fluorochloromethanes
Formic Acid
Hydrazine
Hydrogen Peroxide
Hydrogen
Isopropanol
Isopropylbenzene
Latex
Lead Chromate
Lead Oxides

APPENDIX 1 - (Cont'd)

The Second Group of Priority Chemicals (Cont'd)
(100 substances or groups)

Magnesium Hydroxide
Malathion
Maleic Anhydride
Methyl Ethyl Ketone
Methyl Methacrylate
Methylamines
Methylene Chloride
MCPA
n-Hexane
Nitrilotriacetic Acid
Nitroglycerine
Nonyl Phenol
PCBs
Pentachlorophenol
Pentaerythritil
Perchloroethylene
Phthalic Anhydride
Potassium Hydroxide
Potassium Sulfate
Propylene Glycols
Sodium Aluminate
Sodium Arsenite
Sodium Borohydride
Sodium Carbonate
Sodium Cyanide
Sodium Dichloroisocyanurate
Sodium Dichromate
Sodium Phosphates
Sodium Silicates
Sodium Sulfite
Sulfuryl Chloride
Tall Oil
Terephthalic Acid
Terphenyls
Titanium Dioxide
Triallate Pesticides
Trichlorfon Pesticides
Trifluralin Pesticides
Trinitrotoluene
Turpentine
Vinyl Acetate
Yellow Cake
Zinc Chloride
Zinc Oxide
1,1,1-Trichloroethane
1,2-Butadiene
2,4-D (2,4-Dichlorophenoxyacetic Acid)
2,4-Toluene Diisocyanate

DOE/EPS/EICD/EEB 6 July 1982